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THE MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES. I. FERRIC OXIDE SOL

BY HARRY B. WEISER

Two general theories of the mechanism of the coagulation of sols by electrolytes have been proposed: the adsorption theory of Freundlich and what may be termed the solubility theory of Duclaux and Pauli.

The Adsorption Theory. The widely accepted adsorption theory[1] assumes in the first instance that the particles of hydrophobic sols owe their charge to the preferential adsorption of ions from the intermicellar solution. Thus silver chloride formed in the presence of a slight excess of silver nitrate is positively charged because the particles adsorb silver ion more strongly than nitrate ion whereas silver chloride precipitated with a slight excess of sodium chloride is negatively charged because, in this case, the anion is the more strongly adsorbed. Similarly, hydrous ferric oxide thrown down in the presence of a slight excess of ferric chloride or hydrochloric acid is positively charged because of preferential adsorption of cations. The addition of suitable amounts of electrolytes to such colloidal systems causes coagulation as a result of preferential adsorption of the ions whose charge is opposite to that on the colloidal particles. This adsorption lowers the charge on the particles below a critical value and the colliding particles agglomerate into clumps sufficiently large to settle out. The ions whose preferential adsorption by the sol particles is responsible for their charge are called stabilizing ions while the added ions of opposite charge whose adsorption lowers the particle charge, are called precipitating ions. Since the ions of a precipitating electrolyte which have the same charge as the sol help to determine the critical concentration necessary for coagulation, the precipitation concentration or precipitation value of an electrolyte for a sol has been defined[2] as that concentration which results in sufficient adsorption of the precipitating ion to neutralize below a critical value, the combined adsorption of the original stabilizing ion and that added with the electrolyte. That the precipitating ions are carried down by the coagulated particles was demonstrated first by Linder and Picton[3] and then by Whitney and Ober[4] and has been confirmed repeatedly by a number of investigators.

To account quantitatively for the wide variation in the precipitating power of electrolytes of varying valence, Freundlich assumed that equal amounts of precipitating ions are adsorbed from equimolar solutions and that equivalent amounts of ions of different valence are carried down at the precipitation value. The evidence to support these assumptions was not conclusive and it was demonstrated 10 years ago in the author's laboratory[1] that they are not generally true. Freundlich[2] has recently convinced himself that his original postulates are not in accord with the facts.

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[1] Freundlich: "Kapillarchemie," 1st Ed., 345 (1909); 2nd Ed., 572 (1922).

[2] Weiser and Nicholas: J. Phys. Chem., **25**, 742 (1921).

[3] J. Chem. Soc., **67**, 63 (1895).

[4] J. Am. Chem. Soc., **23**, 842 (1902).

To account for the variation from equivalent adsorption during precipitation of sols, it was assumed[3] that the adsorption of equivalent amounts of the several ions was necessary to neutralize the charge below the critical value and that the observed variation from equivalence was due to varying adsorption of the several electrolytes by the agglomerating micelles. As will be pointed out in the experimental part of this paper, these assumptions are not borne out by the facts.

Since the two ions of the precipitating electrolyte are not adsorbed in equivalent amounts, the adsorption of the precipitating ion must be in part by exchange. Thus Linder and Picton[4] showed that chloride ion passes into solution by exchange when a ferric oxide sol prepared from ferric chloride is coagulated by potassium sulfate; with As_2S_3 sols, hydrogen ion enters the solution by exchange during coagulation.[5]

In concluding this brief survey of the adsorption theory of the coagulation process, it may be said that the theory furnishes a satisfactory semi-quantitative picture of the behavior of sols in the presence of electrolytes, but gives little insight into what actually takes place in any given case.

The Solubility Theory. The solubility theory of the mechanism of the coagulation process probably had its origin in a concept of Wyrouboff[6] that the various dialyzed ferric oxide sols are basic salts or chlorides of "condensed" ferric hydroxides. This idea was further developed by Duclaux[7] and especially by Pauli and his pupils,[8] who consider the stability of sols from the point of view of solubility. The colloidal particles are assumed to be highly complex colloidal ions resulting from the ionization of complex electrolytes allied to the Werner compounds. Coagulation in terms of this theory is believed to consist essentially of a chemical change involving the precipitation of a difficult soluble electrolyte.

Ferric oxide sol formed by adding ammonium hydroxide to ferric chloride solution followed by dialysis, has been investigated extensively from this point of view. Pauli[9] determined the chloride content of the sol by direct analysis and by a potentiometric method and measured the conductivity of the sol at various dilutions. It was found that not all of the chlorine could be detected potentiometrically as chloride ion. The possibility that a part of the chloride was adsorbed[10] and so would not be subject to potentiometric measurement was ruled out and instead, it was assumed that the sol was merely an incompletely dissociated electrolyte which yielded only a fraction of its chlorine as ion.

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[1] Weiser and Middleton: J. Phys. Chem., **24**, 30, 630 (1920).
[2] Freundlich, Joachimsohn, and Ettish: Z. physik. Chem., **141**, 249 (1929).
[3] Weiser and Middleton: Loc. cit.
[4] J. Chem. Soc., **87**, 1908 (1905).
[5] Whitney and Ober: J. Am. Chem. Soc., **23**, 842 (1902).
[6] Bull., **21**, 137 (1899).
[7] J. Chim. phys., **5**, 29 (1907); **7**, 405 (1909).
[8] Pauli and Matula: Kolloid-Z., **21**, 49 (1917); Pauli and Walter: Kolloidchem. Beihefte, **17**, 256 (1923); Pauli and Rogan: Kolloid-Z., **35**, 131 (1924).
[9] Loc. cit.
[10] Cf. Maffia: Kolloidchem. Beihefte, **3**, 85 (1911).

In support of the dissociation theory, Pauli showed that the addition of an electrolyte to the sol which is equally concentrated in chloride ions causes no displacement of the chloride ion concentration of the sol. Moreover, under certain conditions the cations of an added electrolyte with a common anion may also decrease in concentration, a phenomenon which is attributed to a driving back of the dissociation by the common ion of the ferric oxide sol. As Freundlich[1] points out, neither of these arguments is conclusive. For if the chloride ion is in adsorption equilibrium, it is only natural that the equilibrium should be maintained if the chloride ion concentration remains unchanged. Furthermore, the fact that the anions in the intermicellar liquid are sufficiently free to drive back the dissociation of an added salt with a common anion is likewise in entire accord with the adsorption equilibrium which exists in the sol. Finally, Pauli and Matula[2] emphasize that the behavior of sols as regards conductivity cannot be interpreted simply from the point of view of the dissociation theory. Thus a mixture of ferric oxide sol and alkali chloride containing equivalent amounts of chloride ion exhibits a conductivity higher than the arithmetic mean of the conductivity of the components. This is probably due to higher mobility of the colloidal particle owing to an increase in charge by adsorption of a portion of the added cations.

In this connection Lottermoser[3] found the specific conductance of ferric oxide sols to be higher than that of the ultrafiltrates, the differences being regarded as the true conductivity of the micelles. If the micelles *P* are considered to be complex electrolytes, the equivalent conductivity at infinite dilution may be calculated from the equation, $\Delta_{P_\infty} = 1000K_P/K_{Cl}$, where K signifies specific conductance. The mobility of the micelles was found to rise abnormally with purified sols containing but small amounts of chlorine. This fact indicates that the micelles are really adsorption complexes, the abnormality being due to the displacing of the adsorption and hydrolysis equilibria by dilution.

The general formula of a ferric oxide sol is written by Pauli $[xFe(OH)_3.yFeOCl.FeO]^+ + Cl^-$. The addition of sufficient electrolyte such as potassium sulfate, to the sol causes coagulation and the amount of sulfate dragged down is the same as the amount of chloride in the supernatant solution after coagulation. The precipitation is attributed to the formation of a complex insoluble sulfate in accord with the equation $[xFe(OH)_3.yFeOCl.FeO]Cl + K_2SO_4 = [xFe(OH)_3.yFeOCl.FeO]_2SO_4 + 2\ KCl$. Actually, of course, the alleged insoluble sulfate is not thrown down until a critical concentration of sulfate is added. This anomalous behavior as compared with that in the precipitation of simple insoluble compounds calls for an explanation. "The addition of sulfate and similar acting salts to the sol, says Pauli and Walter,[1] "causes precipitation owing to the formation of insoluble compounds. The anomalous behavior as compared to simple electrolytes, namely that an amount of sulfate almost equivalent to the entire chlorine content of the sol is necessary for flocculation, is explained by a peculiar equilibrium between the complex bound and the ionic chlorine as well as by the peptizing action of the undischarged complex. The coagulated sol has the formula of a complex double salt, a chlorine-poor and sulfate-rich chlor-sulfate. The ratio of chlorine to sulfate is in the first instance a function of particle size. It increases with particle size since the analytically determined maximum exchange of chlorine (with excess sulfate) decreases with the growth of the particles." The coagulating action of an alkali chloride is attributed to a driving back of the dissociation of the salt and a similar action is assumed to account for the precipitation with alkali nitrate.

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[1] "Kapillarchemie," 621 (1922).

[2] Kolloid-Z., **21**, 498 (1917).

[3] Z. Elektrochemie, **30**, 391 (1924).

It will be noted that Pauli's interpretation of the coagulating action as a chemical precipitation process, involves the use of the phrases "peculiar equilibrium between the complex bound and the ionic chlorine" and "peptizing action of the undischarged complex." It would be interesting to know just how Pauli visualizes the "peculiar equilibrium" relations and the "peptizing" action referred to.

The general point of view of Pauli is accepted by Wintgen, Rabinowitsch, and others. Considering the micelles to be ordinary ions, Wintgen[2] determines the amount of colloidal substance deposited by one Faraday of electricity and designates this the electrochemical equivalent or "equivalent aggregate" of the colloid. The number of electrochemical equivalents of colloid per liter is called the normality of the colloid, N. This value is obtained by applying Kohlrausch's law, $1000\ K_m = N(u + v)$. K_m the specific conductance of the micelle is estimated from the conductance of the colloidal system before and after ultrafiltration; u the mobility of the colloidal particle is gotten from U-tube measurements; v the mobility of the anion is known, and N is calculated. The similarity between colloidal behavior and ordinary ionic reactions in solution is indicated. Thus colloidal chromic oxide is regarded as an amphoteric electrolyte which reacts with either acids or bases to give salts.[3] It is pointed out that equi-normal colloidal solutions containing oppositely charged particles should mutually precipitate each other.

Whatever merits Wintgen's formulation of the constitution of colloids and the mechanism of the coagulation processes may have, it should be pointed out that his work is vitiated by a methodical error. Laing[4] showed that the fraction of the current carried by any charged body whether ion, colloid, wall, or bubble is equal to the ratio of its actual conductivity to the total conductivity of the system. That is

$$\text{fraction of current} = c_1 f_1/\mu,$$

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[1] Kolloidchem. Beihefte, 17, 291 (1923).

[2] Z. physik. Chem., **103**, 250 (1922); Wintgen and Biltz: **107**, 403 (1923); Wintgen and Löwenthal: **109**, 378 (1924); Wintgen: Kolloid-Z., **40**, 300 (1926).

[3] Wintgen and Weisbecker: Z. physik. Chem., **135**, 182 (1928).

where c_1 is the concentration and f_1 is the conductivity of unit concentration and μ is the sum total of all such *cf* terms for all constituents present. The bodily movement n_1 differs from the above by a factor *m* which is the number of units to one electrical charge. Thus

$$\text{bodily movement} = n_1 = c_1 m_1 f_1/\mu.$$

McBain[1] points out that Wintgen and his pupils neglected this factor *m*. They should have divided their mobilities by m_1 to find the conductivity. A further error was made in interpreting U-tube experiments on cataphoresis. Both Lash Miller and G. N. Lewis showed that the law of conservation of matter requires that the "moving boundary" method must give results which are identical with those derived from the Hittorf method of quantitative analysis. These errors and the neglect of the Donnan equilibrium makes Wintgen's numerical values for the charges on the particles something like ten times too large.

If one insists on regarding ferric oxide sols merely as electrolytes with complex ions it must be emphasized that there is a fundamental difference between sols and non-colloidal complex electrolytes such as potassium ferrocyanide, the cobalt amines, the complex platinous salts, etc. formulated by Werner. There is also a distinct difference between a colloidal ferric oxide and such colloidal electrolytes as the soaps and Congo red in that the latter contains ionic micelles made up of groups of ions of definite composition and carrying one charge for each equivalent of the ion, whereas the micelle of the former has no definite composition and may carry hundreds or thousands of equivalents for each free charge.

In conclusion, there seems no justification for assuming the absence of adsorption in a system such as colloidal ferric oxide where an adsorption equilibrium between minute solid particles of hydrous ferric oxide and the surrounding solution, must certainly exist.

It was believed that further light could be thrown on the structure of colloidal systems and the mechanism of coagulation by following the change in composition on adding a precipitating electrolyte stepwise to a sol. Since the precipitating ion is taken up in exchange with chloride in ferric oxide sol prepared from ferric chloride solution, Rabinowitsch and Kargan[2] followed the change in the chloride ion concentration potentiometrically on adding sulfate and other ions stepwise to a measured portion of the sol. The procedure was as follows: A 20 cc portion of sol in which was some suspended calomel, was placed in a beaker containing mercury thus making one half of a calomel concentration cell. The other half was a saturated calomel electrode. The difference in potential was found with a potentiometer at the outset and shortly after each addition of a small amount of electrolyte. From the potential measurements, the concentration of chloride ion at each step was calculated using the Nernst equation. Typical curves obtained by Rabinowitsch for the titration of two different sols with N/2 sodium sulfate are given in Fig. 1. The straight line represents the concentration of sulfate added while the irregular curves represent the changing concentration of chloride. It will be noted not only that the curves are irregular but that they run above the sulfate line indicating that considerably more chloride is displaced than there is sulfate added. Indeed special attention is called to the observation that

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[1] Colloid Symposium Monograph, **4**, 14 (1926).

[2] Z. physik. Chem., **133**, 203 (1928).

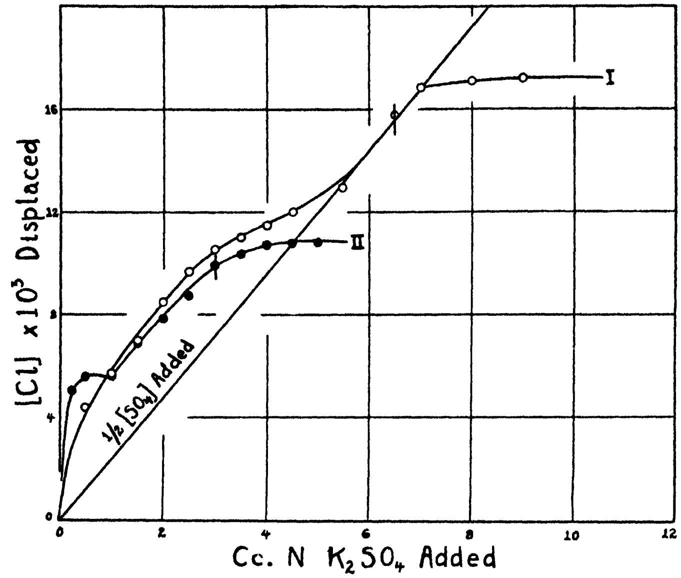

Fig. 1
Titration curves of Fe_2O_3 sols with K_2SO_4 (from data by Rabinowitsch and Kargan)

0.05 cc N/2 Na_2SO_4 displaced more than 4.6 times the equivalent of chloride in one sol. There is no apparent reason for this behavior and Rabinowitsch's explanation of it is not satisfactory. Moreover, as will be discussed later on, Rabinowitsch and Kargan either do not give all the facts or there is some error in their calculations of chloride concentrations from the observed potentials. In any event, the general method seemed to offer a fruitful method of approach to the problem of what takes place when an electrolyte is added to a sol. The results of investigations along this line are reported in the next section.

Experimental

Preparations of Sols. Three ferric oxide sols were used in the course of this investigation. The first was prepared by dissolving 100 grams of pure ferric chloride in approximately 500 cc of water, filtering, and adding dilute ammonia just short of precipitation. The concentrated sol was diluted to 4 liters and dialyzed in four Neidle dialyzers using cellophane bags which held approximately one liter. The dialysis proceeded with a continuous change of water for two days when the chlorine content was found to be approximately

0.015 normal. The sol was set aside in a pyrex flask for four months before using. The second sol was prepared by the same procedure outlined above except that the ageing following the dialysis was accomplished by heating for a week on the steam hot-plate. Loss by evaporating was prevented by attaching a reflux condenser to the mouth of the flask. This sol was used within a month after preparation. The third sol was formed by dissolving 75 grams of ferric chloride in 500 cc of water and adding slowly to 3500 cc of boiling water. After dialysis at 90° for two days, the sol was set aside for three months before using.

The sols were analyzed for the Fe_2O_3 content and the chlorine content as follows: The ferric oxide in 25 cc portions of the sols was coagulated by ammonia and the precipitate was collected, washed, ignited and weighed in the usual manner. The chlorine content of 25 cc portions of sol was obtained by first adding a small excess of silver nitrate followed by adding nitric acid and heating. This process dissolved the oxide leaving a precipitate of silver chloride. After diluting, the silver salt was collected in a Gooch crucible, dried and weighed. The analyses are given in Table I.

TABLE I

Analysis of Ferric Oxide Sols

Sol number	Fe_2O_3 grams per liter	Cl mols per liter
I	6.46	0 0158
II	6.92	0.0166
III	4.08	0 0047

Method of Titration. Preliminary experiments disclosed quite promptly that satisfactory data could not be obtained by adding the electrolyte to the sol stepwise and measuring the change in chloride ion potentiometrically after a few minutes. The reason is obvious when one considers that it takes time to establish equilibrium at the calomel electrode. Indeed it is always recommended that the newly prepared standard calomel half element be set aside at least a day and preferably several days before use. Accordingly the procedure adopted by Rabinowitsch and Kargan was discarded as unsatisfactory and the following method adopted: In general, the method consists in mixing separate portions of sol with gradually increasing amount of electrolyte and making the observations on the separate samples. In the sol was suspended a small amount of freshly precipitated calomel. This was prepared by the interaction of pure mercurous nitrate and hydrochloric acid followed by thorough washing with the aid of the centrifuge in the presence of a small amount of mercury, first with water and then with the sol. To secure rapid uniform mixing of the sol with electrolyte 20 cc of the former was placed in the outer compartment of an all-glass mixing apparatus and a definite amount of electrolyte diluted to 5 cc in the inner compartment. After mixing, the mixture was transferred to a small bottle which was placed in the thermostat at 25° and shaken at intervals for a period of two days in order to saturate with calomel. It was then transferred to an electrode vessel like that shown in Fig. 2. This was prepared by rounding out the bottom of a 30 cc weighing bottle to prevent its breaking, followed by sealing in a small platinum wire. After placing mercury in the bottom of the vessel, the sol-electrolyte mixture was poured in and allowed to stand in the thermostat 24 hours before making the potentiometric measurements. Thus an interval of three days elapsed between the mixing of sol with electrolyte and the determination of the chloride ion content.

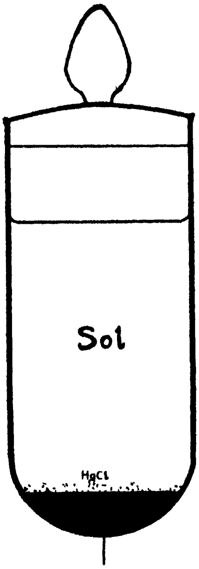

Fig. 2

Potentiometric Measurements. The potentiometric measurements were made by means of a N/10 calomel electrode prepared in the usual way from highly purified potassium chloride, calomel, and mercury. Contact between the standard electrode vessel and the "unknown" was made directly by the aid of a glass tube filled with the N/10 KCl and drawn down to a fine capillary to minimize diffusion. A type K Leeds and Northrop potentiometer was used in conjunction with a Hartman and Braun moving coil galvanometer sensitive to less than 0.1 millivolt.

Calculations. From the observed potential the molar concentration of chloride as potassium chloride was obtained by the use of the modified Nernst equation substituting activities for concentrations. At 25° the activity coefficient of N/10 KCl is 0.749[1] and the equation takes the form $\pi = 0.0591 \log 0.0794/\alpha$. The calculated value of α is converted into molar concentration by dividing it by the corresponding activity coefficient as read off from a graph prepared from data given by Lewis and Randall.[2]

In this connection, attention should be called to an apparent error in the calculations of Rabinowitsch and Kargan. For example, a potential of 0.1589 volts at 19° using a saturated calomel electrode as a standard was calculated to give a chloride ion concentration of 0.00794 mol per liter. The activity coefficient of such a solution is 0.933 and the activity is thus 0.00741. Substituting this value in the Nernst formula at 19° and solving for the activity of the chloride in saturated KCl at 19°, one gets:

$$0.1589 = 0.0579 \log \frac{\alpha_{\mathrm{KCl\ Sat.}}}{0.0074}$$

from which, $\alpha_{\mathrm{KCl\ Sat.}} = 4.11$.

Now the difference between the potential of the saturated and N/10 calomel electrode at 19° is approximately 0.0874 volt.[3] To give this potential the activity of the chloride in the saturated half element is given by the equation

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[1] Lewis and Randall: "Thermodynamics," 362 (1923).

[2] "Thermodynamics," 344 (1923).

[3] Clark: "The Determination of Hydrogen Ions," 200 (1927).

$$0.880 = 0.0579 \log \frac{\alpha_{\mathrm{KCl\ Sat}}}{9.0794}$$

from which $\alpha_{\mathrm{KCl\ Sat}} = 2.63$. Since the value for α which Rabinowitsch and Kargan must have used is more than 60 per cent higher than the above, their concentrations calculated from the observed potentials would appear to be erroneous.

In this connection Rabinowitsch and Kargan report the same value for the total chlorine in the sol by gravimetric analysis as silver chloride after dissolving the precipitate in nitric acid, and by potentiometric analysis of the supernatant solution after adding a precipitating electrolyte. Since ferric oxide sol prepared according to the procedure employed by Rabinowitsch and Kargan contains chlorine that is not displaced by a coagulating electrolyte, the two methods should not yield the same results. That they did is most likely the result of some compensating error in the potentiometric procedure.

Observations on Ferric Oxide Sol I

Titration with K_2SO_4. After a number of preliminary experiments which led to the procedure described above, the following observations were made of the change in chloride concentration on adding varying amounts of N/25 K_2SO_4 to the sol. Above the precipitation value of the salt, the suspended calomel was carried down completely by the agglomerating oxide. In order to make certain that the supernatant solution was saturated with Hg_2Cl_2 a small amount of calomel paste was added after the coagulation had taken place. The results of the titration are given in Table II and shown graphically in Fig. 3.

TABLE II

Titration of Fe_2O_3 Sol I with K_2SO_4

Cc of N/25 K_2SO_4 added to 20 cc of sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to [SO_4] added $\times 10^3$
0.0	0.0857	2.82	2.93	0	0
0.5	0.0834	3.08	3.20	0.27	0.80
1.0	0.0800	3.52	3.68	0.75	1.60
1.5	0.0768	4.00	4.20	1.27	2.40
2.0	0.0746	4.34	4.57	1.64	3.20
2.5	0.0725	4.71	4.96	2.03	4.00
2.0	0.0707	5.05	5.34	2.41	4.80
3.5	0.0686	5.48	5.81	2.88	5.60
4.0	0.0674	5.75	6.10	3.17	6.40
4.5	0.0616	7.11	7.60	4.67	7.20
4.75	0.0608	7.43	7.95	5.02	7.60
5.00	0.0592	7.91	8.47	5.54	8.00
2.5 of N/10	0.0582	8.22	8.82	5.89	10.00

Referring to the data and the accompanying curve, it is obvious that the chloride displaced during the titration follows a regular course. Particularly significant is the fact that the amount of chloride displaced is always appreciably less than the amount of sulfate added, contrary to the observation of Rabinowitsch and Kargan. Since the sol was prepared by essentially the same procedure and was similar in oxide and chloride content to the one used by them, it seems probable that their experimental method led to erroneous observations. Attention has already been called to possible errors in their calculations.

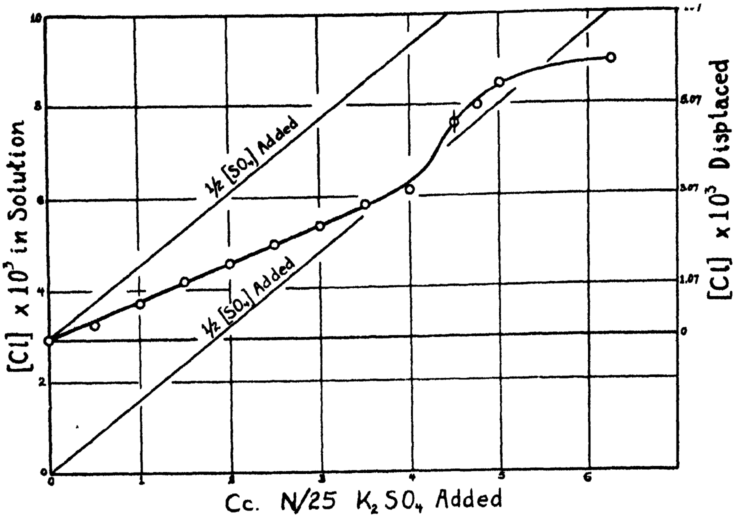

FIG. 3
Titration curve of Fe_2O_3 Sol I with K_2SO_4

It is of interest to note that the curve for chloride displaced follows a nearly linear course until the precipitation concentration is approached when it increases rapidly. Above the precipitation concentration, indicated by a vertical line cutting the curve, the chloride displaced follows the usual adsorption type of curve.

The precipitation concentration 4.5 cc of N/25 K_2SO_4 in 25 cc was the smallest amount of electrolyte which would just cause complete coagulation in three days.

At the precipitation concentration, the supernatant solution gave no test for sulfate with barium chloride even after several days. Since the "sulfate added" comes quite close to the "chloride" curve at the precipitation value, it is clear that the amount of sulfate adsorbed is approximately equivalent to the chloride in the supernatant solution, as Pauli has demonstrated.

Since all the added sulfate is taken up at the precipitation value, it is reasonable to conclude that all of it is taken up below the precipitation value. It is of particular importance to note that at the precipitation value as well as at all points above and below the precipitation value, the chloride equivalent to the sulfate added is derived in part from the chloride originally present in the intermicellar solution and in part is displaced from the micelles. This behavior will be considered in detail in a later section.

The marked increase in the chloride displaced as the precipitation concentration is approached is undoubtedly the result of partial agglomeration of particles with the consequent decrease in specific surface as the charge approaches the critical value below which complete flocculation takes place.

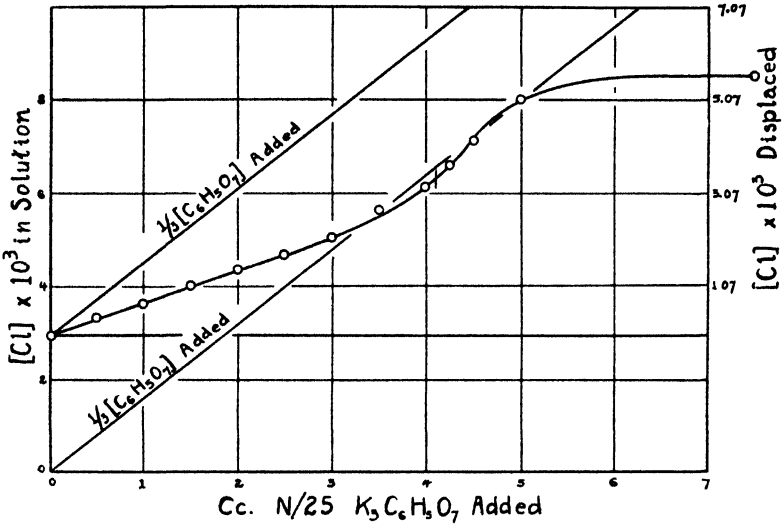

FIG. 4
Titration curve Fe_2O_3 Sol I with potassium citrate

Finally, the form of the upper portion of the "chloride" curve represents the adsorption of sulfate by precipitated ferric oxide in concentrations above the precipitation value, since the sulfate taken up is approximately equivalent to the chloride in solution. Attention has been called to this behavior in earlier communications.[1]

Titration with $K_3C_6H_5O_7$. Experiments with N/25 potassium citrate were carried out by the same procedure used for potassium sulfate. The data are recorded in Table II and shown graphically in Fig. 4. It is evident that the displacement of chloride by citrate follows a course strikingly similar to that for sulfate. The only difference is the earlier upward turn in the curve and the lower precipitation concentration of the salt as indicated in the figure. The maximum amount of chloride displaced above the precipitation value is almost identical in the two cases.

Titration with $K_3Fe(CN)_6$. Since $K_3Fe(CN)_6$ which is the salt of a strong acid might be expected to give largely trivalent anions, it was of interest to compare the behavior of the sol during the stepwise addition of this salt

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[1] Weiser: J. Phys. Chem., **25**, 299 (1921); Weiser and Middleton: **24**, 30, 630 (1920).

TABLE III

Titration of Fe_2O_3 Sol I with Potassium Citrate

Cc of N/25 $K_3C_6H_5O_7$ added to 20 cc of sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to $[C_6H_5O_7$ added $\times 10^3$
0.0	0.0857	2.82	2.93	0.0	0.0
0.5	0.0823	3.22	3.36	0.43	0.80
1.0	0.0805	3.45	3.61	0.68	1.60
1.5	0.0777	3.85	4.04	1.11	2.40
2.0	0.0758	4.16	4.38	1.45	3.20
2.5	0.0740	4.44	4.68	1.75	4.00
3.0	0.0723	4.75	5.01	2.08	4.80
3.5	0.0692	5.36	5.69	2.76	5.60
4.0	0.0674	5.75	6.10	3.17	6.40
4.25	0.0655	6.19	6.58	3.65	6.80
4.50	0.0636	6.66	7.10	4.10	7.20
4.00[1]	0.0606	7.49	8.01	5.08	8.00
7.50[1]	0.0592	7.91	8.48	5.55	10.91

[1] Sol repeptized, with negative charge.

with that of citrate which doubtless gives some trivalent anions but divalent and monovalent anions as well. The titration data are given in Table IV and the curve in Fig. 5. The potentiometric measurements for chloride are very satisfactory so long as practically all of the added salt is adsorbed, but the measurements are uncertain as soon as an appreciable amount of ferricyanide remains in the supernatant solution.

The curve for displacement of chloride by ferricyanide is characterized by the earlier upward bend and the distinctly lower precipitation value as

TABLE IV

Titration of Fe_2O_3 Sol I with $K_3Fe(CN)_6$

Cc of N/25 $K_3Fe(CN)_6$ added to 20 cc of sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to $[Fe(CN)_6]$ added $\times 10^3$
0.0	0.0857	2.82	2.93	0.0	0.0
0.5	0.0828	3.17	3.31	0.38	0.80
1.0	0.0801	3.50	3.66	0.73	1.60
1.5	0.0777	3.85	4.04	1.11	2.40
2.0	0.0742	4.41	4.65	1.72	3.20
2.5	0.0717	4.86	5.13	2.20	4.00
3.0	0.0693	5.34	5.66	2.73	4.80
3.25	0.0674	5.75	6.10	3.17	5.20
3.50	0.0655	6.19	6.58	3.65	5.60
4.00	0.0630	6.82	7.27	4.34	6.40
5.00	Uncertain				

compared with both sulfate and citrate. Since all the ferricyanide and sulfate are carried down at the respective precipitation values and since the precipitation value in equivalents of the former is appreciably lower than that of the later, it is obvious that Freundlich's assumption that equivalent amounts of all ions are carried down at the precipitation value cannot be right. My later assumption that the adsorption of equivalent amounts is necessary to lower the charge to the coagulation point, likewise is not generally true. The total chloride in the intermicellar liquid near the precipitation value and after coagulation, appears somewhat greater than the ferricyanide added. This is because coagulation with consequent decrease in specific surface starts at very low concentrations and so the displaced chloride is relatively greater for ferricyanide than for other salts at the same concentration. At the same time, it should be noted that there is appreciably less chloride displaced and total chloride in the supernatant solution at the lower precipitation value of $K_3Fe(CN)_6$ than at the higher value for K_2SO_4.

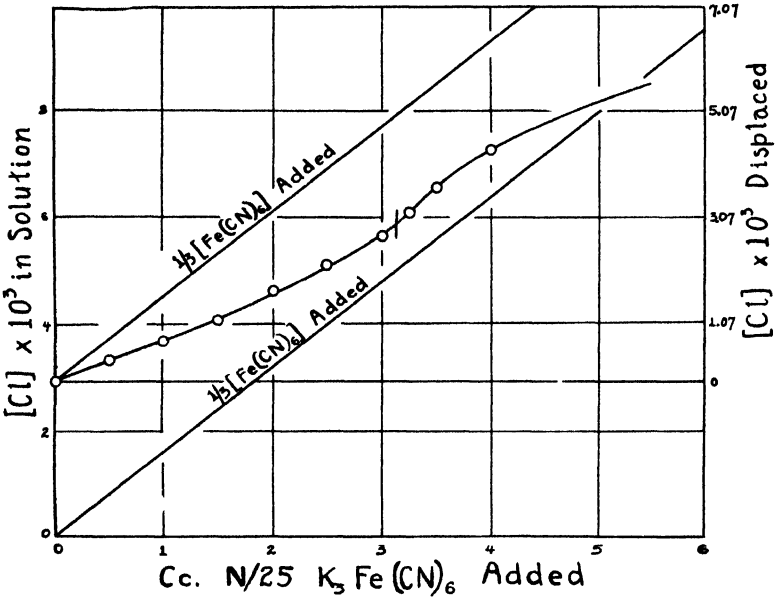

Fig. 5
Titration curve of Fe_2O_3 Sol I with $K_3Fe(CN)_6$

Titration with KNO_3. Since univalent anions in general precipitate positive sols only in relatively high concentration, it was necessary to use a normal solution of KNO_3 to effect the coagulation within 5 cc of electrolyte in 25 cc of mixture. In the interest of accuracy N/10 solutions were used for lower concentrations. The titration data given in Table V are plotted in Fig. 6. The form of the curve is distinctly different from that for salts with multivalent precipitating ions. The amount of chloride displaced for the same concentration is very much less for the univalent ion. Moreover the

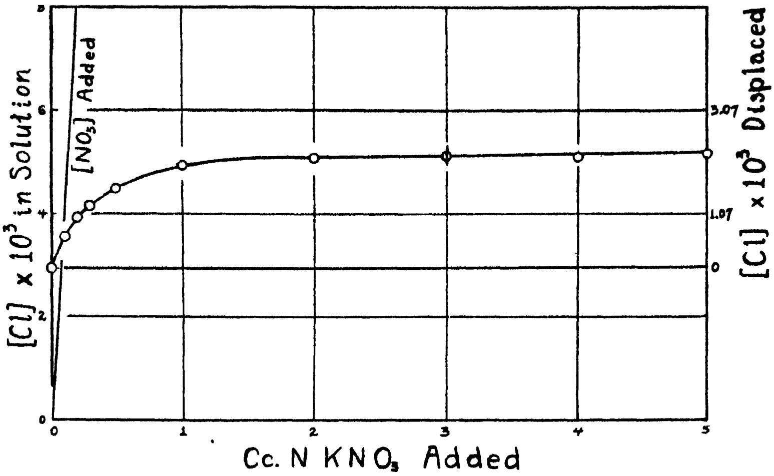

FIG. 6
Titration curve of Fe_2O_3 Sol I with KNO_3

amount of chloride displaced goes up fairly rapidly at relatively low concentrations but soon attains a practically constant value or even decreases slightly. The latter observation may be the result of a salt error introduced with relatively high concentrations of KNO_3. In any event, the maximum amount of chloride displaced is appreciably less for nitrate than for the multivalent ions.

The variation in the chloride displacing power of equivalent amounts of potassium salts of mono-, di-, and trivalent anions is clearly indicated in the composite diagram Fig. 7.

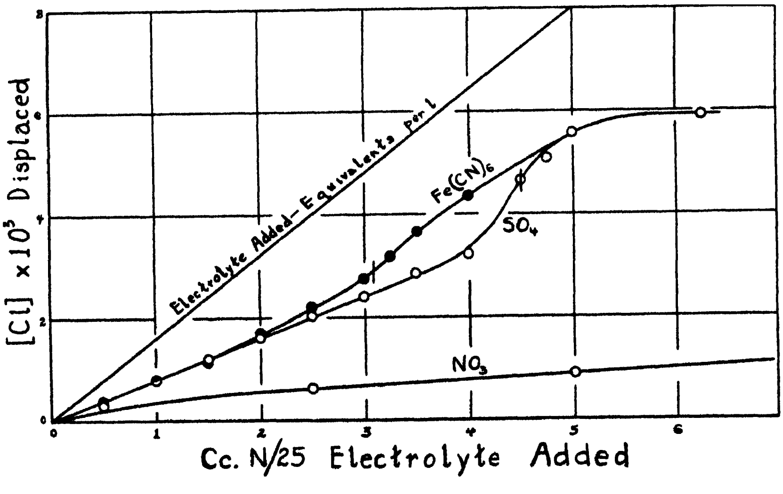

FIG. 7
Titration curves of Fe_2O_3 Sol I with different types of electrolytes

TABLE V

Titration of Fe_2O_3 Sol I with KNO_3

Cc of KNO_3 added to 20 cc of Sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	$[Cl]$ $\times 10^3$	$[Cl]$ displaced $\times 10^3$	$[Cl]$ equivalent to $[NO_3]$ added $\times 10^3$
0	0.0857	2.82	2.93	0.0	0.0
1 of N/10	0.0812	3.37	3.53	0.60	4.0
2 of N/10	0.0785	3.73	3.91	0.98	8.0
3 of N/10	0.0772	3.92	4.12	1.19	12.0
5 of N/10	0.0750	4.27	4.49	1.53	20.0
1 of N	0.0728	4.66	4.92	1.99	40.0
2 of N	0.0720	4.81	5.08	2.15	80.0
3 of N	0.0718	4.84	5.11	2.18	120.0
4 of N	0.0722	4.76	5.03	2.10	160.0
5 of N					200.0

Experiments with Ferric Oxide Sol II

Sol II was prepared in much the same way as Sol I but was aged by heating instead of by long standing. The results with the former merely confirm and extend those with the latter.

Titration with K_2SO_4. The data for the titration with potassium sulfate is given in Table VI and shown graphically in Fig. 8. As compared with Sol I, it will be noted that the curve starts to bend upward at a lower concentration and the precipitation value is somewhat lower. As was to be expected the general form of the curve is the same as with Sol I.

TABLE VI

Titration of Fe_2O_3 Sol II with K_2SO_4

Cc of K_2SO_4 added to 20 cc. of Sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	$[Cl]$ $\times 10^3$	$[Cl]$ displaced $\times 10^3$	$[Cl]$ equivalent to $[SO_4]$ added $\times 10^3$
0.0	0.0910	2.29	2.37	0.0	0.0
0.5	0.0880	2.58	2.69	0.32	0.80
1.0	0.0843	2.98	3.11	0.74	1.60
1.5	0.0804	3.48	3.64	1.27	2.40
2.0	0.0778	3.83	4.02	1.65	3.20
2.5	0.0748	4.31	4.54	2.17	4.00
3.0	0.0727	4.67	4.93	2.56	4.80
3.5	0.0700	5.19	5.49	3.12	5.60
4.0	0.0675	5.73	6.07	3.70	6.40
4.25	0.0647	6.38	6.68	4.31	6.80
4.50	0.0626	6.93	7.40	5.03	7.20
5.00	0.0605	7.52	8.04	5.67	8.00
6.25	0.0597	7.76	8.31	5.94	10.00

In order to test the accuracy of the experimental procedure for determining chloride potentiometrically, an analysis was made of the supernatant solution after precipitation. This was done by precipitating 40 cc of sol with 10 cc of N/25 K_2SO_4 and analyzing an aliquot part of the supernatant solution for chloride by titrating with silver nitrate. The silver nitrate was standardized against N/50 silver chloride and the titrations were made to the same end-point. The results given in Table VII show the potentiometric procedure to be quite accurate.

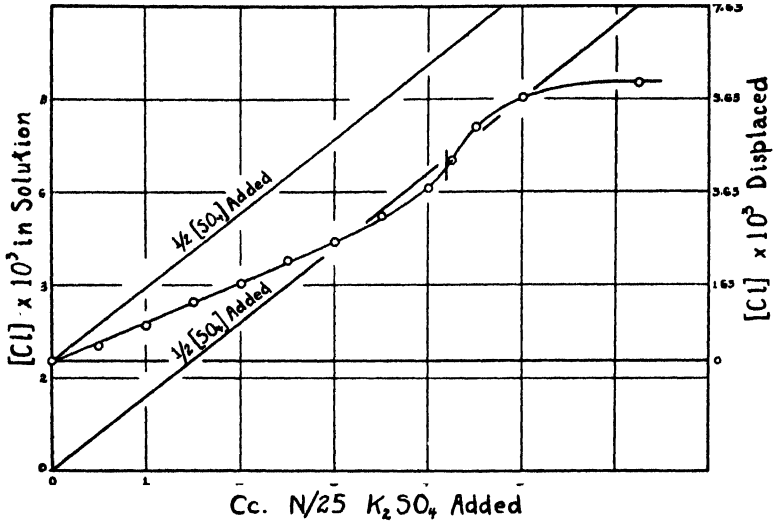

FIG. 8
Titration curve of Fe_2O_3 Sol II with K_2SO_4

TABLE VII
Analysis of Supernatant Solution for Chloride after Precipitation Fe_2O_3 Sol II

Substances mixed		0.001934 N $AgNO_3$ to titrate 25 cc	[Cl] × 10³	
Fe_2O_3 Sol cc	N/25 K_2SO_4 cc	cc	volumetric method	potentiometric method
40	10	10.48	8.16	8.10
40	10	10.45	8.08	8.04
Fe_2O_3 Sol	N/25 K_2CrO_4			
40	10	10.80	8.40	
40	10	10.80	8.40	

Titration with $K_2C_2O_4$. The data and corresponding curves with $K_2C_2O_4$ as precipitating electrolyte are given in Table VIII and Fig. 9, respectively. The upper portion of the curve with $K_2C_2O_4$ runs slightly above that with K_2SO_4 and the precipitation concentration of the former is slightly lower than the latter. As in the case of sulfate, all of the oxalate is adsorbed at the precipitation value.

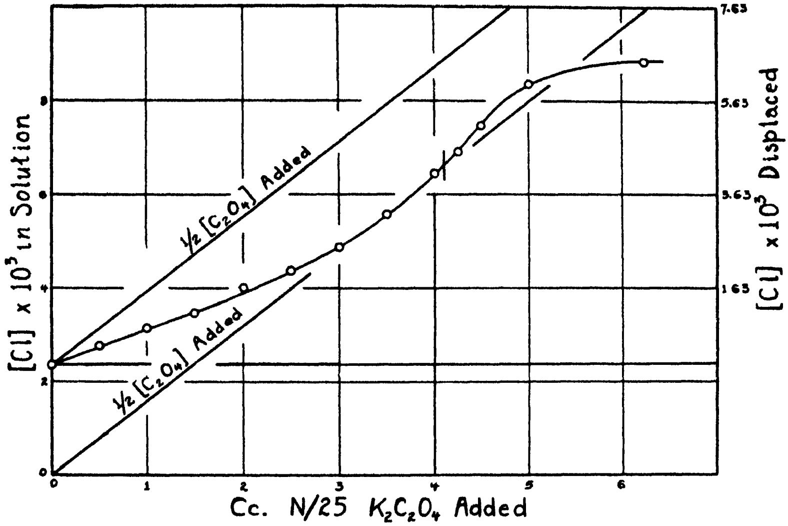

FIG. 9
Titration curve of Fe_2O_3 Sol II with $K_2C_2O_4$

TABLE VIII

Titration of Fe_2O_3 Sol II with $K_2C_2O_4$

Cc of N/25 $K_2C_2O_4$ added to 20 cc of Sol. Total volume 25 cc.	π volts	a Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to $[C_2O_4]$ added $\times 10^3$
0.0	0.0910	2.29	2.37	0.0	0 0
0.5	0.0875	2.66	2.77	0 40	0.80
1.0	0.0840	3.01	3.14	0 77	1 60
1.5	0.0815	3 32	3.47	1.10	2.40
2.0	0.0778	3.83	4.02	1.65	3.20
2.5	0.0758	4.15	4.36	1.99	4.00
3.0	0.0730	4.62	4.87	2.50	4.80
3.5	0.0697	5.25	5.56	3.19	5.60
4.0	0.0660	6.07	6 45	4 08	6.40
4.25	0.0643	6.48	6.90	4.53	6.80
4 50	0.0623	7.01	7.47	5 10	7 20
5.00	0 0595	7.81	8.36	5 99	8.00
6.25	0.0583	8.22	8.82	6.45	10.00

Titration with K_2CrO_4. The data using K_2CrO_4 as precipitating electrolyte and the corresponding curve are given in Table IX and Fig. 10. The curve parallels that obtained with $K_2C_2O_4$ almost throughout the entire range and the observed precipitation concentration lies between the values for oxalate and sulfate. All of the chromate is carried down at the precipitation value. Satisfactory potentiometric measurements were not obtained with appreciable concentrations of K_2CrO_4 in the supernatant solution above

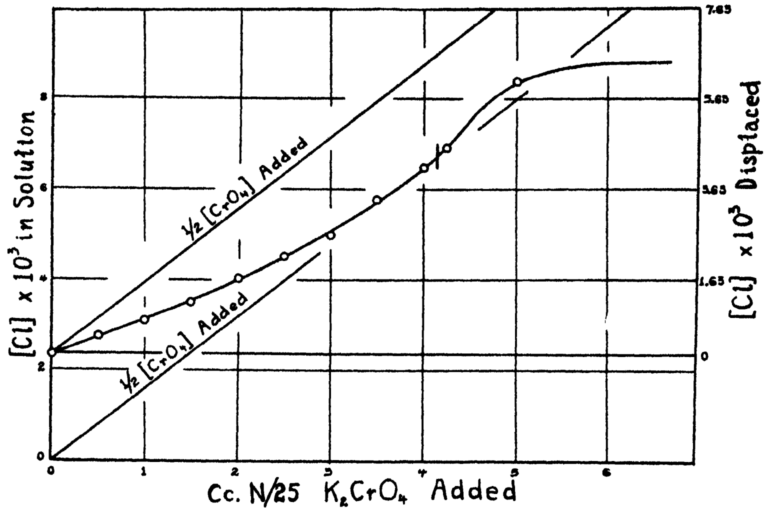

FIG. 10
Titration curve of Fe_2O_3 Sol II with K_2CrO_4

the precipitation value. The point for 5 cc N/25 K_2CrO_4 with 20 cc of sol was obtained by volumetric analysis of the supernatant solution with the results as given in the second part of Table VII. The value 8.40×10^{-3} mols per liter corresponds with 8.36×10^{-3} obtained potentiometrically with oxalate as precipitating electrolyte.

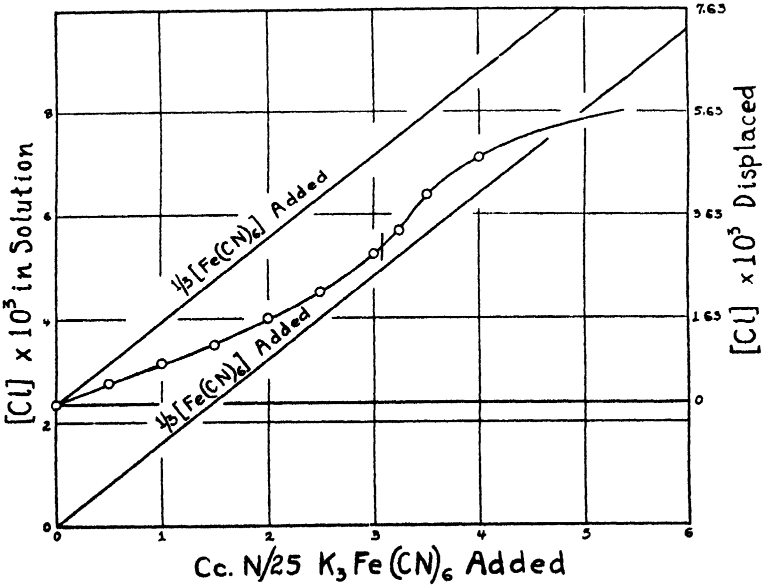

FIG. 11
Titration curve of Fe_2O_3 Sol II with $K_3Fe(CN)_6$

TABLE IX

Titrations of Fe_2O_3 Sol II with K_2CrO_4

Cc of N/25 K_2CrO_4 added to 20 cc. Sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to [CrO_4] added $\times 10^3$
0.0	0.0910	2.29	2.37	0.0	0.0
0.5	0.0875	2.66	2.77	0.40	0.80
1.0	0.0845	2.95	3.08	0.71	1.60
1.5	0.0812	3.35	3.50	1.13	2.40
2.0	0.0775	3.87	4.07	1.70	3.20
2.5	0.0746	4.34	4.55	2.18	4.00
3.0	0.0725	4.71	4.97	2.60	4.80
3.5	0.0686	5.49	5.81	3.44	5.60
4.0	0.0658	6.12	6.50	4.13	6.40
4.25	0.0643	6.48	6.90	4.53	6.80
5.00	—	—	8.40[1]	6.03	8.00

[1] Determined analytically, (See Table VII).

Titration with $K_3Fe(CN)_6$. The observations with $K_3Fe(CN)_6$ as precipitating electrolyte merely confirm those obtained with Sol I. The data are given in Table X and shown graphically in Fig. 11.

TABLE X

Titrations of Fe_2O_3 Sol II with $K_3Fe(CN)_6$

Cc of N/25 $K_3Fe(CN)_6$ added to 20 cc. of Sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to [$Fe(CN)_6$] added $\times 10^3$
0.0	0.0910	2.29	2.37	0.0	0.0
0.5	0.0870	2.68	2.79	0.42	0.80
1.0	0.0842	2.99	3.12	0.75	1.60
1.5	0.0815	3.32	3.47	1.10	2.40
2.0	0.0778	3.83	4.02	1.65	3.20
2.5	0.0750	4.27	4.50	2.13	4.00
3.0	0.0712	4.96	5.24	2.87	4.80
3.25	0.0692	5.36	5.68	3.31	5.20
3.50	0.0662	6.02	6.40	4.03	5.60
4.00	0.0637	6.65	7.09	4.72	6.40
5.00	Uncertain				8.00

The results of the observations on Sol II are collected in Fig. 12. It is of interest to note the marked similarity in the behavior of the salts with divalent anions. The precipitation concentrations are quite close together and the chloride concentrations of the respective supernatant solutions are almost identical. Since the adsorption of the multivalent anions observed is complete at the precipitation value, Freundlich's assumption that equivalent amounts of ions are adsorbed at the precipitation concentration holds almost

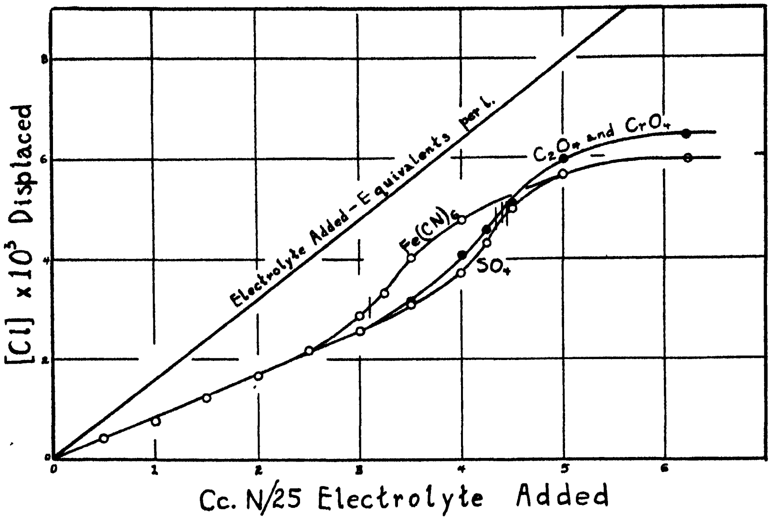

FIG. 12
Titration curves of Fe_2O_3 Sol II with different types of electrolytes

quantitatively for the three ions under consideration. But when one turns to trivalent ferricyanide, one encounters a distinctly lower equivalent precipitation value and correspondingly lower adsorption at the precipitation value, confirming the observation with Sol I.

Observations with Ferric Oxide Sol III

Sol III prepared by hydrolysis of $FeCl_3$ in hot water and dialyzed in the hot was much freer from chloride than either Sol I or II. Moreover, since no ammonia was added, the sol contained simply the hydrolysis products of $FeCl_3$, hydrous Fe_2O_3 and HCl. That its behavior on titrating with K_2SO_4

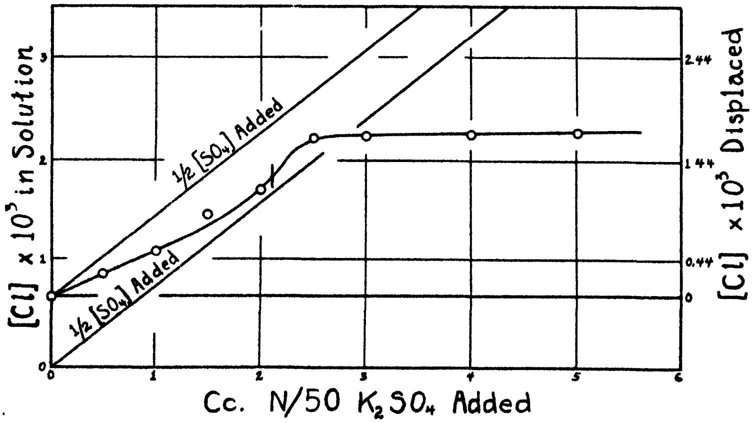

FIG. 13
Titration curves of Fe_2O_3 Sol III with K_2SO_4

is similar in all respects to that observed with less pure sols obtained by somewhat different procedures, is shown by the data given in Table XI and plotted in Fig. 13.

TABLE XI

Titration of Fe_2O_3 Sol III with K_2SO_4

Cc of N/50 K_2SO_4 added to 20 cc. of Sol. Total volume 25 cc.	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[Cl] equivalent to $[SO_4]$ added $\times 10^3$
0.0	0.1220	0.69	0.70	0.0	0.0
0.5	0.1154	0.91	0.93	0.23	0.40
1.0	0.1097	1.11	1.14	0.44	0.80
1.5	0.1025	1.47	1.51	0.81	1.20
2.0	0.0994	1.66	1.71	1.01	1.60
2.5	0.0926	2.15	2.23	1.53	2.00
3.0	0.0925	2.16	2.24	1.54	2.40
4.0	0.0924	2.17	2.25	1.55	3.20
5.0	0.0922	2.19	2.27	1.57	4.00

Discussion of Results

A theory of the mechanism of the coagulation of colloidal ferric oxide must explain the following facts reported in the preceding section:

1. At the precipitation value of potassium salts of multivalent ions the chloride in the supernatant solution is equivalent to or but little greater than the amount of added electrolyte.

2. Only a part of the chloride that is found in the supernatant solutions after precipitation, can be detected potentiometrically in the original sol before adding electrolyte. Not all of the chloride in the micelles is displaced by a large excess of precipitating electrolyte.

3. The chloride measured potentiometrically following the stepwise addition of electrolyte, consists of the chloride in the sol originally, together with an additional amount that is displaced when the added anion is taken up.

4. The multivalent ions investigated are taken up practically completely by the sol particles in concentrations up to and including the precipitation concentration. The chloride displaced so that it can be detected potentiometrically, is less than half the amount equivalent to the multivalent ion taken up.

5. The amount of chloride displaced follows nearly a linear course at the outset of the stepwise addition of multivalent ions but becomes proportionately greater as the precipitation concentration is approached.

6. The chloride displacement curves for multivalent ions of varying valence follow an almost identical course until the precipitation concentration is approached when there is a marked divergence for ions of different valence.

7. The three salts of divalent anions exhibit a strikingly similar behavior as regards the entire course of the chloride displacement curves and the precipitating power.

8. The trivalent ferricyanide coagulates at a distinctly lower concentration than the divalent ions and the chloride displaced at the precipitation value is proportionately less with the former than with the latter.

9. The chloride displacement curve with potassium salts of univalent ions such as nitrate, follows a course distinctly lower than that for the multivalent ions.

The solubility theory of Pauli would attempt to explain all of these facts on the basis of metathetical reactions with the formation of insoluble salts of the added electrolytes. Even if one disregards the objections to the theory which have been referred to already, the Pauli mechanism appears inadequate to account for the observations. A few cases may be mentioned. First of all, it seems altogether improbable that the alleged complex salts of such widely varying anions as sulfate, oxalate, and chromate should all possess practically the same solubility and so precipitate at the same concentration of added electrolyte. Nor is there any reason for supposing that the solubility of the alleged complex trivalent ferricyanide and citrate should be appreciably less than that of the divalent complexes. Moreover, it is difficult to explain on the basis of solubility relationships, why potassium oxalate and potassium ferricyanide, say, which must be assumed to form salts of widely varying solubility, should give chloride displacement curves which follow an almost identical course until the precipitation concentration of the trivalent ion is approached. Finally, I do not think that the time has yet arrived when anything can be gained by applying the term salt to a complex formed when a positively charged particle of variable composition takes up a given negative ion in varying amounts depending upon the conditions of preparation of the particle.

An adsorption mechanism which will now be outlined appears to offer a more rational interpretation of the facts: When ferric chloride is hydrolyzed there are formed positively charged micelles which vary in size, composition, and charge, depending on the conditions of the hydrolysis. In general, the colloidal particle exclusive of the outer layer has a composition represented by some point in the three-component diagram, Fe_2O_3-HCl-H_2O which may be represented symbolically $[xFe_2O_3.yHCl.zH_2O]$. This indicates the observed fact that there is chloride within the micelle which is not displaced even by high concentrations of precipitating electrolytes. It also indicates what is well known, that the actual composition of the particle is determined by its method of formation and the subsequent history.

Assume for the sake of simplicity that the hydrolysis has taken place to the point where the electrolyte active in sol formation is HCl and not $FeCl_3$. Now the finely divided solid particles of $xFe_2O_3.yHCl.zH_2O$ exhibit such a marked tendency to adsorb hydrogen ion as compared with chloride that the sols prepared as described above are almost neutral having a pH value of 6 to 6.5 whereas an appreciable concentration of chloride ion is observed potentiometrically. If n represents the number of hydrogen ions adsorbed by the micelle and q equals the chloride concentration of the sol that can be measured potentiometrically, the composition of the sol may be formulated as follows:

$[x\mathrm{Fe_2O_3}.y\mathrm{HCl}.z\mathrm{H_2O}]\mathrm{H}^+_n.n\text{-}q\mathrm{Cl}^- + q\mathrm{Cl}^-$. This is represented diagrammatically in Fig. 14 in which the inner layer of the double layer surrounding the particle is composed of the adsorbed hydrogen ions. The outer portion of the double layer is a diffuse layer[1] consisting of an equivalent amount of chloride ions as shown. Some of the chloride ions because of their relatively higher kinetic energy exert sufficient osmotic repulsive force against the electrical attraction of the H^+ ion layer, to influence the calomel electrode and are therefore detected potentiometrically. Such ions are represented in the diagram beyond the dotted circle.

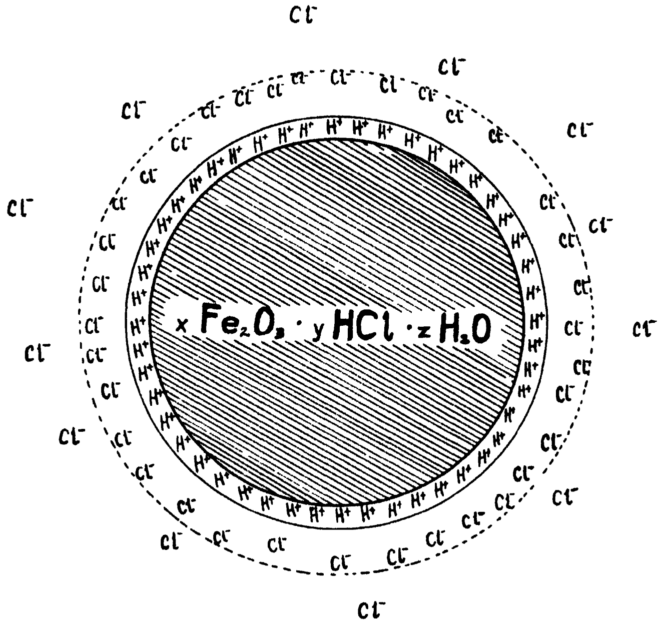

Fig. 14
Diagrammatic representation of the structure of the micelle in a ferric oxide sol.

When potassium sulfate is added to the sol, the more strongly adsorbed divalent sulfate ion forces itself into the double layer closer to the adsorbed hydrogen ion and displaces chloride as indicated diagrammatically in Fig. 15. Potentiometric analysis enables one to determine the chloride which has been displaced. The difference between the chloride in the sol originally and that after the addition of sulfate, in other words, the displaced chloride is not equivalent to the adsorbed sulfate since a part of the sulfate which enters the layer corresponds to chloride measurable potentiometrically in the original sol.

The adsorbed sulfate lowers the charge on the particle in the following way: A sulfate ion possesses the same average kinetic energy as a chloride ion but it possesses double the charge. Accordingly, if one assumes for the moment that the valence only determines the adsorbability, the divalent particles in the outer layer would be drawn closer to the inner layer and the thickness of the double layer would be decreased. Since the potential difference between two layers of opposite sign with constant charge density is directly proportional to the distance between them, it follows that the reduced thickness of the layer will be accompanied by a decrease in charge on the particle.

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[1] Gouy: J. Phys., (4) 9, 457 (1910).

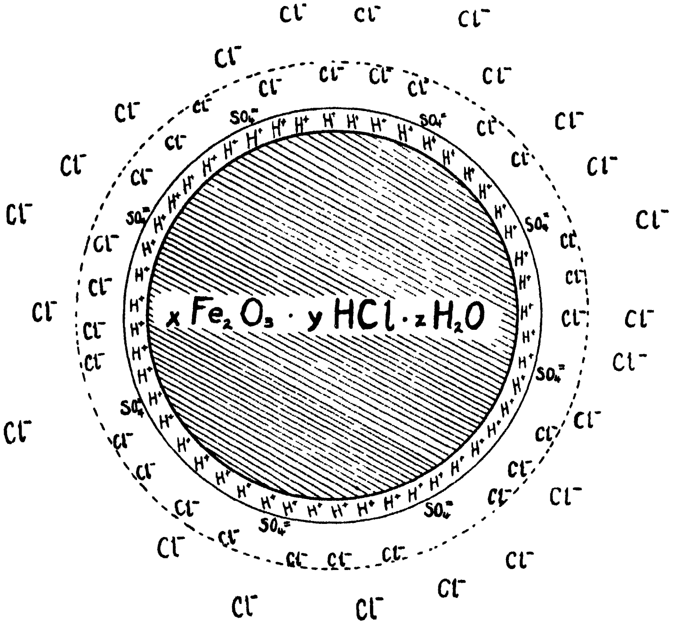

FIG. 15
Diagrammatic representation of the structure of the micelle in a ferric oxide sol after adding some K_2SO_4

Since the three divalent ions sulfate, oxalate, and chromate exhibit such a strikingly similar behavior in displacing chloride and in reducing the charge to the critical coagulation value, it follows that in the case of these three ions the valence is the most important factor determining the adsorbability.

The behavior of trivalent ions such as ferricyanide would follow from what has been said. The ions having the same average kinetic energy but with three charges will be drawn closer to the inner layer than the divalent ions and the further reduction in thickness of the double layer manifests itself in a lower precipitation value. The chloride ion displaced is obviously less since less ferricyanide needs to be adsorbed to lower the charge on the particles to the critical coagulation value.

The adsorption of both the divalent and trivalent ions is sufficiently great that the amount added to cause coagulation is practically completely adsorbed. The adsorption at this concentration is not completely irreversible however, since shaking the precipitated gel with water results in partial repeptization of the sol owing to some of the precipitating ions breaking away from the close adsorption layer.

The increase in the chloride displaced for a given increment in the multivalent ion added in the region of the precipitation value, is the result of agglomeration and partial coalescence of the colloidal particles into micelles having a lower specific surface for a given mass.

The behavior of nitrate ion as compared with multivalent ions might be inferred from what has gone before. A much higher concentration of the univalent ions is necessary to produce the same effect as the multivalent ions since the latter are attracted so much more strongly toward the adsorbed hydrogen ion and so would be expected to effect the necessary lowering of charge in much lower concentration. The smaller amount of chloride displaced by nitrate as compared with the multivalent ions is not surprising in view of the fact that chloride is quite as effective as nitrate in lowering the charge. There is some chloride displaced because the higher concentration of nitrate causes some of the latter to enter the double layer and force out an equivalent amount of chloride.

Summary

The following is a brief summary of the results of this investigation.

1. A procedure is described for accurate potentiometric determination of the change in chloride concentration on adding electrolytes stepwise to hydrous oxide sols containing a slight excess of hydrochloric acid or ferric chloride as stabilizing electrolyte.

2. Only a part of the chloride that is found in the supernatant solution after coagulation can be detected potentiometrically in the original sol before adding electrolyte. The chloride measured potentiometrically following the stepwise addition of electrolyte, consists of the chloride in the sol originally together with an additional amount that is displaced when the added anion is taken up.

3. Titration curves are given which show the increase in chloride ion concentration on adding potassium sulfate, chromate, oxalate, ferricyanide, and nitrate stepwise to different ferric oxide sols.

4. The multivalent anions are taken up practically completely by the sol particles in concentrations up to and including the precipitation concentration. The chloride displaced so that it can be detected potentiometrically is less than half the amount equivalent to the multivalent ion taken up. At the precipitation value, the chloride in the supernatant solution is equivalent to or but little greater than the amount of multivalent ion added.

5. The titration curves follow a nearly linear course at the outset of the stepwise addition of multivalent anions but the amount of chloride displaced for a given increment of precipitating ion is relatively greater as the precipitation concentration is approached. Above the precipitation concentration, the curves take the form of an adsorption isotherm.

6. For simple multivalent ions of the same valence, the titration curves are strikingly similar. For multivalent ions of varying valence there is a marked divergence. Thus trivalent ferricyanide coagulates at a distinctly lower concentration than divalent sulfate and the chloride displaced at the precipitation value is proportionately less with the former than with the latter. The titration curve with a univalent precipitating ion such as nitrate follows a course distinctly lower than that for the multivalent ions.

7. In ferric oxide sols such as those under consideration the composition of the micelle exclusive of the outer layer is given by some point in the three component diagram Fe_2O_3-HCl-H_2O which may be represented symbolically as $xFe_2O_3.yHCl.zH_2O$. This indicates the observed facts that there is chloride within the micelle which is not displaced by electrolytes and that the composition varies with the conditions of preparation and the subsequent history of the sample.

8. The outer capsule of the micelle which largely determines its colloidal properties consists of an ionic double layer. The inner portion is adsorbed hydrogen or ferric ions; the outer portion is a diffuse layer consisting of chloride ions most of which are held by the electrical attraction of the adsorbed positive layer while others because of relatively higher kinetic energy exert sufficient osmotic repulsive force against the inner layer, to influence the calomel electrode and are therefore detected potentiometrically.

9. An adsorption mechanism is outlined to account for the change in composition and nature of the double layer which results in a decrease in charge on the micelle when electrolytes are added to the sol. At the same time, the proposed mechanism accounts for the form of the chloride displacement curve with different electrolytes.

10. The mechanism outlined accounts for the observed fact that relatively less of a trivalent ion must be adsorbed than of a divalent ion in order to lower the charge on a particle to the critical coagulation potential.

11. The relative merits of the proposed adsorption mechanism of the coagulation process and the solubility theory of Pauli are discussed.

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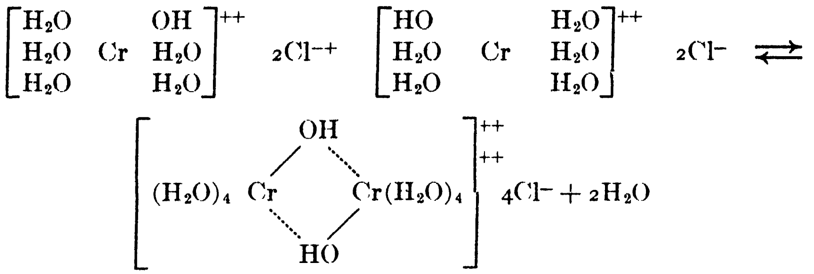
ION INTERCHANGES IN ALUMINUM OXYCHLORIDE HYDROSOLS*

BY ARTHUR W. THOMAS AND THOMAS H. WHITEHEAD

The behavior in solution of many complex inorganic salts (particularly those of cobalt, nickel, chromium, and aluminum) is such that the application of hydrolytic dissociation formulae does not successfully account for this behavior in most instances. Among the several hypotheses formulated to account for the experimental facts, the Werner theory has been successful and consistent in accounting for results obtained and for the prediction of probable behavior of related salts in solution.

The original classical postulates of Werner made in 1893 have since been extended by Pfeiffer, Bjerrum, and Stiasny. The explanation of hydrolysis in Werner terms was made by Pfeiffer shortly after Werner published his first papers.

Bjerrum,[1] in 1907, found it impossible to interpret the results obtained by heating basic chromic sulfate solutions by hydrolytic dissociation formulae. In addition to this, he found that the molecular weight of these salts had increased in some cases to as high as 750. He therefore postulated that perhaps the hydroxo groups in the complex ions were becoming more firmly bound to form larger complexes, such as,—


H₂O OH H₂O Cr H₂O H₂O H₂O ++ 2Cl⁻ +
HO H₂O H₂O Cr H₂O H₂O H₂O ++ 2Cl⁻ ⇄
OH
(H₂O)₄ Cr Cr(H₂O)₄
HO
++ ++ 4Cl⁻ + 2H₂O

Bjerrum called this process "olation." It accounts for decreased activity of hydroxo groups toward neutral salts and sluggishness of attaining equilibrium.

Stiasny,[2] in order to account for decreased activity of basic chromic salts toward neutral salt solutions and decreased solubility of basic chromic salts when they were heated for long periods of time, further extended the idea of Bjerrum to include the conversion of hydroxo groups to oxygen bridges in the complex ion with formation of acid. This process is called "oxolation,"—

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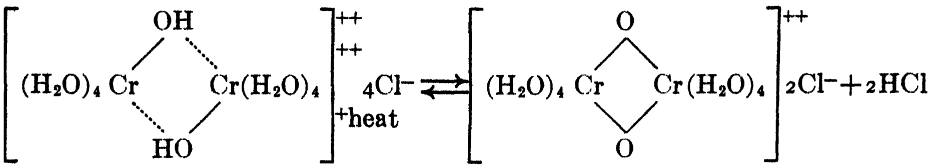
* Contribution from the Department of Chemistry, Columbia University, No. 637.

[1] Bjerrum: Z. physik. Chem., **59**, 336 (1907); "Studier over Basike Kromiforbindelser," Kopenhagen (1908), through Stiasny and Grimm: Collegium **691**, 505 (1927); Z. physik. Chem., **73**, 724 (1910).

[2] Stiasny and Grimm: Collegium, **691**, 505 (1927).



Stiasny[3] also found that the addition of neutral sodium sulfate to basic chromic sulfate solutions decreased the hydrogen ion activity and analysis of the resulting salts showed that the anion of the added sodium sulfate had become a part of the basic chromium salt. He found also that different anions had different degrees of effectiveness in decreasing hydrogen ion activity but in each case the added anion was found in the complex chromium salt. He therefore postulated an equilibrium between basic chromium salt ion and anion, being different for each particular anion and shifted by increasing the concentration of anion with respect to concentration of complex basic ion. This process he called "anion penetration," for example,—

$$\begin{bmatrix} H_2O & & H_2O \\ H_2O & Cr & Cl \\ H_2O & & H_2O \end{bmatrix}^{++} 2Cl^- + KC_2H_3O_2 \rightleftarrows \begin{bmatrix} H_2O & & H_2O \\ H_2O & Cr & C_2H_3O_2 \\ H_2O & & H_2O \end{bmatrix}^{++} 2Cl^- + KCl$$

An outstanding extension of these hypotheses is to be found in the papers by Gustavson[4] on the elucidation of the complex process of tanning leather by chrome liquors.

The large molecular aggregates obtained by Bjerrum with basic chromic salts led the authors to believe that perhaps particles of colloidal size might be built up in this manner, and, if so, they should act similarly to the basic chromic salts toward heating, aging, and neutral salt solutions.

The object of the present investigation was to apply the above mentioned hypotheses to the explanation of the behavior of aluminum oxychloride hydrosols made in the hot (80°-70°C) toward ageing and neutral salts and to attempt to give some picture of these hydrosols in terms of these hypotheses.

Materials

The C P aluminum chloride hexahydrate used yielded the following results upon analysis: Al = 99.50 per cent of theoretical; Cl = 99.40 per cent of theoretical; Fe = 0.01 per cent; Sulfate = Less than 0.002 per cent.

Ammonium hydroxide, C P.

Sodium hydroxide, C P,—a saturated solution was prepared and let stand for one month. Aliquots were siphoned from this and diluted.

The distilled water was always boiled just previous to use. All reagents after being prepared were kept in "NonSol" glass bottles. Pyrex ware was used in preparation of reagents.

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[3] Stiasny and Szego: Collegium, **670**, 41 (1926).

[4] J. Am. Leather Chem. Assocn., **18**, 568 (1923); **21**, 22, 53 (1926); **22**, 68 (1927); Collegium, **672**, 153 (1926).

The potassium chloride, bromide, iodide, nitrate, and sulfate were twice recrystallized from boiling distilled water and dried at 110°C for twelve hours.

Potassium oxalate was dried at 110°C for three hours. It was tested for chlorides, sulfates, and heavy metals according to Murray[5] and found to be satisfactory. Its oxalate content was tested by titration against a standard solution of potassium permanganate which had been standardized the day before against sodium oxalate from the Bureau of Standards. Calculated on the basis of the formula $K_2C_2O_4.H_2O$ the oxalate content was 99.90 per cent of the theoretical.

Ammonium acetate was tested according to Murray[5] for chlorides, sulfates, and heavy metals. None was found, so the salt was simply dried over calcium chloride in a desiccator for two weeks.

Preparation of Sols

The general method of preparation was to dissolve 10 grams of aluminum chloride hexahydrate in two liters of water at 20°C. Alumina hydrate was then precipitated by addition of ammonium or sodium hydroxide at 20°C and the whole immediately heated to the desired temperature. (This must not exceed 80°C because it was found that above 80°C the alumina hydrate changes from its greyish color to a white color and becomes very much less soluble.) The mixture was kept hot for two hours and then allowed to cool to 20°C. The alumina hydrate settled out. The supernatant liquor was siphoned off and the precipitate washed with hot distilled water (70°C). After washing, the desired amount of distilled water was added and whole mechanically stirred while the minimum amount of hydrochloric acid necessary to peptize was added. (This amount was determined by preliminary preparation of similar sols.) The mixture was again heated (to same temperature as at first) for two hours, put in a "NonSol" bottle and allowed to stand for 24 hours, after which it was centrifuged for one hour at 1500 r.p.m. (Rotating radius to middle of tube was 42 cm) The supernatant liquor was carefully siphoned off (if any sediment had formed) after standing for 24 hours, and again centrifuged at 1500 r.p. m. for one hour. When nothing was thrown out after one hour centrifuging at 1500 r.p.m., the sol was considered peptized.

This method gave results which were reproducible and offered a means of making aluminum oxychloride hydrosols of a wide range of alumina hydrate concentration.

Four sols were selected varying in concentration of alumina hydrate content, in the temperature at which they were prepared, and in the precipitating reagent. These preparations were considered colloidal because they conformed to criteria which have been cited as being characteristic of the colloidal state; that is

(a) They did not dialyze through nitrocellulose membranes either at 20°C or at 80°C over a period of three days, although HCl in them did.

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[5] "Standards and Tests for Reagent Chemicals," 276 (1920).

(b) They exhibited a Tyndall cone in the carbon arc slit ultra-microscope.

(c) They appeared turbid but did not settle out under gravity over a period of six months or in a centrifuge at 840 times gravity in one hour.

(d) The adition of various salt solutions resulted in precipitation of the dispersed phase.

Analyses of Sols

Aluminum[6], *Total.* Since there were no other interfering elements present except a slight trace of iron, aluminum could be precipitated as the hydrate with ammonium hydroxide, filtered off, and ignited to the oxide.

To 100 cc of sol, 10 cc of glacial acetic acid were added and the whole left on the steam plate until solution was effected, usually about two hours. This solution was then made faintly alkaline with ammonium hydroxide (to methyl red) and allowed to digest over night at 20°C. It was filtered through Whatman No. 44 filter paper, washed twice with distilled water, and filter paper with precipitate transferred to a previously ignited quartz crucible, heated on an air bath till paper was completely charred, then ignited over a Meker flame for one hour, cooled in desiccator and weighed to the nearest 0.5 milligram.

Aluminum, Ionic. No evidence of any aluminum ion was obtained by use of the aluminon test[7] for which a sensitivity of 10^{-5} mol/l aluminum ion is claimed.

Chlorine, Total.[8] One hundred cc of sol and 10 cc of 18 M nitric acid with not more than 10 per cent excess over calculated amount of 0.1 M solution of silver nitrate solution were put on steam plate, covered with watch glass, and allowed to stand for 10 hours in a dark room. After cooling, the silver chloride was filtered off by means of a porous bottom Gooch crucible and heated in an oven at 115°C for three hours. This method had previously been verified in this laboratory by Hamburger in the analysis of ferric oxybromide hydrosols.[9]

Chlorine, Ionic. Chloride ion was determined directly on the sol by taking 100 cc of sol, adding 25 cc of distilled water and 3 cc of 0.1 M potassium chromate. Tenth molar nitric acid was added dropwise till the orange color of bichromate ion was seen, then 1 gram of powdered calcium carbonate[10] was added followed by titration with 0.1 M silver nitrate solution.

Ammonia, Total. The standard Kjeldahl method for nitrogen as ammonia was used to determine total ammonia in the sols.

Ammonium Ion. After solution of the sol has been effected, ammonium ion was determined by use of the Nessler reagent, as prescribed by the American Public Health Association method.[11]

To do this, 2 cc of 0.5 M potassium oxalate solution were added to 50 cc of sol and it was allowed to stand over night and filtered through Whatman

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[6] Hillebrand and Lundell: "Applied Inorganic Analysis," 389 (1929).

[7] Hammett and Sottery: J. Am. Chem. Soc., 47, 142 (1925).

[8] Fales: "Inorganic Quantitative Analysis," 196 (1924).

[9] Hamburger: Dissertation, "A Study of Ferric Oxybromide Hydrosols," Columbia University (1926).

[10] Hillebrand and Lundell: Loc. cit., 590.

[11] "Standard Methods of Water Analysis," 16, 17.

No. 44 filter paper. The precipitate was washed carefully with ten portions of 5 cc each of distilled water, allowing the washings to go into the filtrate. Aliquots of 5 cc each were pipetted out, diluted to 100 cc, 2 cc Nessler reagent added and the color compared with a standard solution by means of a Duboscq type colorimeter. Determinations were run in triplicate and results checked to 0.5 milli-equivalent.

Measurement of Hydrogen Ion Activity

Since it has been established[12] that the quinhydrone electrode gives reliable results between pH 2 and 7.5, this electrode was chosen for use in this investigation. It is interesting to note also that Pelling[13] found the quinhydrone electrode valid for measuring the pH values of aluminum sulfate solutions (0.001 M to 0.4 M).

Electrode Vessel. This was a 125 cc glass, wide mouth, bottle fitted with a rubber stopper admitting electrode, salt bridge, and air stirrer.

Platinum Electrodes. The electrodes were made of bright platinum wire sealed into a glass tube and the tube filled with redistilled mercury. Two were made and constantly checked against each other. It was necessary often to leave them over night in 18 M nitric acid to get consistent and reliable results.

Salt Bridge. The salt bridge was a glass U-tube with stop-cock in the center. The side arms were of equal length and plugged with cotton to prevent diffusion of sol into salt solution, which occurred unless this precaution was taken. The bridge was filled with saturated potassium chloride solution (at 25°C) and the stop-cock kept closed. The stop-cock was well covered with graphite.

Air Stirrer. This was simply a glass tube tapered off to small opening at one end and connected through a calcium chloride tube to the source of compressed air by rubber tubing.

Calomel Half-cell. Two saturated KCl calomel cells were made according to Findlay.[14] They were checked against each other constantly and against a standard cadmium cell at intervals.

The electrode vessels were immersed in a water thermostat at 25°C ±0.1°C and the potentiometric readings were taken to the nearest millivolt which was deemed sufficiently accurate for the purpose of this investigation.

Measurement of the Sign of the Electric Charge

The apparatus used was the same as that used by Sherman, Thomas, and Caldwell[15] for measuring the iso-electric point of malt amylase. A diagram with detailed description of parts is given in that paper.

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[12] LaMer and Parsons: J. Biol. Chem., **57**, 613 (1923); Biilmann: Ann. chim., **15**, 109 (1921).

[13] J. Chem. Met. Mining Soc. S. Africa, **26**, 88 (1925).

[14] "Practical Physical Chemistry," 200 (1928).

[15] J. Am. Chem. Soc., **46**, 1711 (1924).

The bottom of the U-tube was filled with sol, the stop-cocks closed and the side arms washed out with distilled water, drained thoroughly, and filled with 0.01 M KCl solution. The electrode vessels were then inserted, the leveling stop-cock opened and the level of the potassium chloride solution allowed to adjust itself; then the leveling stop-cock was closed. The current, 110 volts DC, was then turned on and both large stop-cocks opened simultaneously. The current was allowed to stay on for 24 hours, after which both large stop-cocks were simultaneously closed, the current cut off and the electrode vessels removed. The contents of each side arm were transferred to clean dry beakers, thoroughly stirred and 20 cc portion pipetted out of each and analysed for aluminum.

The colloidal aluminum micelles migrated to the cathode in each case.

Summary of the Properties of Sols

The data concerning the four aluminum oxychloride hydrosols are given in Table I. All figures are in milli-equivalents per liter.

Table I

1 Sol*	2 Temp. of prepn.	3 Total Al	4 Total Cl	5 Cl ion	6 Total NH_3	7 NH_4 ion	8 pH
A	80°	44	1.2	1.22	1.0	1	4.51
B	80°	70	54.90	53.04	. .	48	4.50
C	70°	44	8.67	8.56	8.15	8	4.68
D	70°	62	13.40	13.30	. . .	0	4.39

* In the cases of sols A, B, and C ammonium hydroxide was used to precipitate the hydrous alumina from the original aluminum chloride solution, while sodium hydroxide was employed in the case of the alumina formed for the preparation of sol D.

None of the hydrosols gave any reaction for aluminum ion so that the amounts of aluminum given in column three of Table I were bound up in the complex ionic micelle, which as previously mentioned was cationic in each sol.

It may be seen from columns four and five that nearly all of the chlorine present was in the form of chloride ion, the difference being the amount in the complex aluminum ionic micelle. The analytical methods used were equally precise, and the authors think the differences are significant and not the result of different methods of analysis. In the case of ammonia, however, the slight differences shown in columns six and seven are perhaps due to difference in methods and the authors believe that all of the ammonia was present as ammonium ion.

The results in column eight of the table show slight differences in acidity. This is to be expected because the pH depends upon so many factors, *e.g.*, temperature of preparation, age of the sol, aluminum salt concentration, amount of hydrochloric acid used in peptization of the sol, etc., and since no final state of equilibrium had been reached in any case, no definite relation between the pH and other values was expected.

TABLE II

Effect of Ageing at 20°C on pH of Sols

Time	Sol A	Sol B	Sol C	Sol D	Solution $AlCl_3$*
1 hour					4·44
24 hours	4·54	4·56		4·39	4·42
7 days	4·54	4·59		4·41	4·39
14 days				4·41	4·37
30 days	4·63		5·39		
45 days	4·75	5·42	5·49		

* $AlCl_3$ solution —5 grams $AlCl_3.6H_2O$ per liter solution.

The results listed in Table II show that in all cases the hydrogen ion activity of the sols was decreased upon aging at 20°C. This was found to be the case also for chromium salt solutions which had been heated, but those which had not been heated increased in hydrogen ion activity.[16] The last column in Table II shows that the aluminum chloride solution which had not been heated increased in hydrogen ion activity upon ageing. Thomas and Baldwin[17] found similar results with chromium salt solutions at 20°C.

The decrease in hydrogen ion activity of the sols is therefore significant because all the factors involved would apparently lead to increased hydrogen ion activity; namely, loss of water due to slow evaporation, and slow hydrolysis of the aluminum salt.[18]

An explanation for this phenomenon is given later.

Effect of Heat on pH of the Sols

Fifty cubic centimeters of each sol were put in "NonSol" bottles[19] and left in an oven at 80°C for four days, when they were removed, cooled to 25°C, and the pH measured. There was no loss of volume of the sols during this treatment. The results are given in Table III.

TABLE III

Sol	Original pH	After 3 hours	After 4 days
A	4·75	No change	4·65
B	4·61	No change	4·15
C	5·39	No change	5·22
D	4·39	No change	4·09

These results are very significant. They show obviously that heating increases the hydrogen ion activity, but the greater significance is that upon cooling back to 25°C, the hydrogen ion activity did not decrease to its former value as do salt solutions which undergo hydrolytic dissociation. Hydrolytic dissociation alone then will not account for these results. It should also be noted that heating for only three hours had no measurable effect. This again indicates that hydrolysis is not all that is involved inasmuch as heat increases the hydrolytic dissociation of salts. This behavior of the sols will be explained later.

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[16] Stiasny and Grimm: Collegium, **694**, 49 (1928).

[17] J. Am. Leather Chem. Assocn., **13**, 192 (1918).

[18] Tian: Compt. rend., **172**, 1179 (1921).

[19] Sols heated at 80° for four days in ordinary glass reagent bottles became alkaline to phenolphthalein.

Effect of Neutral Salts on pH of the Sols

All salt solutions were made up just prior to use. Solutions were all at 1 normal concentration.

In the case of potassium oxalate which was alkaline, sufficient 0.5 molar oxalic acid was added to make the solution slightly acid. This did not, however, alter the concentration of oxalate ion available for reaction, as the solution was maintained 0.5 molar with respect to oxalate ion.

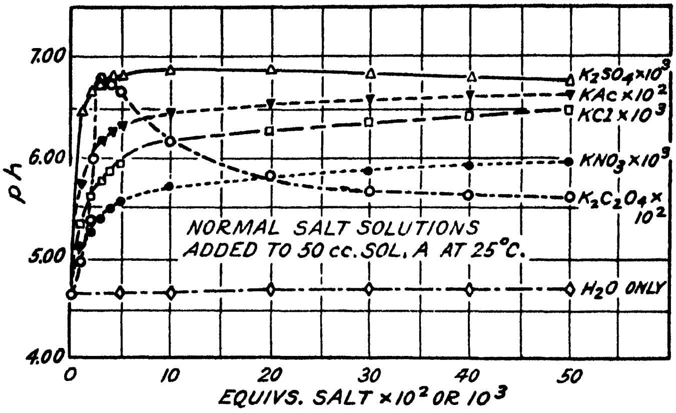

Fig. 1

The pH of the salts solutions at 25°C was:

Salt	KCl	KBr	KI	KNO_3	K_2SO_4	NH_4OOCCH_3	Oxalate
pH	5.44	6.71	7.00	5.86	5.55	7.10	5.07

Technique. The electrode vessel was rinsed with the sol, then 50 cc added with pipette. Half an hour was allowed for saturation by the quinhydrone; readings on the potentiometer taken every five minutes until constant. Usually they became constant in fifteen minutes. Then the salt solution was delivered into the electrode vessel by burette in 1 cc portions (except acetate and oxalate) and potentiometer readings taken after each addition until constant. After 10 cc had been added in this way, the size of portions was increased to 5 cc and added to a total of 50 cc. In the case of acetate and oxalate solutions, the portions were one-tenth the size of the other salt solutions. All solutions except oxalate gave constant readings on the potentiometer within five minutes, so that the readings reported for oxalate are those taken exactly five minutes after its addition. The drift was probably due to some oxidation-reduction reaction in which oxalate ion is notoriously sensitive.

Several facts are evident from the results shown in Table IV and plotted in Fig. 1.

In the first place, it will be seen that all salt solutions increased the pH of sol A, but their magnitudes are different, oxalate and acetate having a ten times greater effect than the other salt solutions. This suggests a chemical reaction between the sol and salt solutions. This is further borne out by the fact that water alone had practically no effect on pH; the effect of the salt solutions then was not due to dilution of the sol by addition of dilute salt solution.

The question might arise as to whether this effect is due to the action of salt on the hydrogen ion activity shown by Harned[20] for solutions of hydrochloric acid. In the case above described, the effect is too great to be accounted for in such a manner.

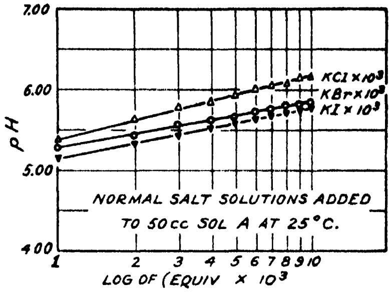

FIG. 2

It is significant that in no case did the pH go above 7. A maximum was reached with oxalate, acetate, and sulfate after which the pH increased because the salt solutions had a pH of 5.22, 7.02, and 5.55 respectively. This maximum is thought to mark the end of the chemical reaction.

That there was no salt effect on the quinhydrone which could be measured was shown by the fact that the pH of the salt solutions was independent of the volume measured. The authors believe that the pH changes obtained upon titration of the sol with the salt solutions are real and not due to "salt effects" upon the quinone-hydroquinone ratio.

It should be noticed that the order of effectiveness of the anions is :

Nitrate < chloride < sulfate < acetate < oxalate.

In Fig. 2 the concentration of salt solution is plotted logarithmically and the slopes of the lines represent the effectiveness of each salt in decreasing the hydrogen ion concentration. It is obvious that all three salts are of very nearly the same effectiveness. For this reason, potassium chloride is taken as typical of the halogen salts and used as such in comparisons with other salts.

The pH changes upon titration of the four sols and of aluminum chloride solution are shown in Table VI and in Fig. 3.

This graph shows first of all that potassium chloride increased the pH of all four sols in a similar manner, but had greater effect upon the sols of low aluminum content (A and C) than upon the sols of high aluminum content

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[20] J. Am. Chem. Soc., 44, 2729 (1922).

(B and D). A similar trend will be noticed with other salts. It is of more than passing interest to point out that sol D was made with sodium hydroxide while B was made with ammonium hydroxide, yet they act alike, indicating that a decrease in hydrogen ion activity is not the result of ammino groups reacting with hydrogen ion. This is further confirmed by the fact that sol A contained only 1 milli-equivalent of ammonia, while sol C contained 26, yet they acted alike.

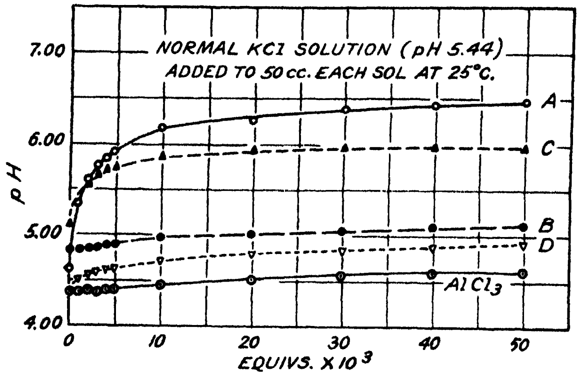

FIG. 3

TABLE IV

50 cc Sol A and 1 Normal Salt Solutions
(Figures are pH values at 25°C)

Cc added	H_2O only	KNO_3	KCl	K_2SO_4	Cc	NH_4Ac	$K_2C_2O_4$
0	4.75	4.75	4.75	4.75	0.0	4.75	4.75
1	4.77	5.13	5.39	6.47	0.1	5.75	4.99
2	4.78	5.28	5.63	6.69	0.2	6.00	5.39
3	4.78	5.42	5.80	6.73	0.3	6.19	6.77
4	4.78	5.51	5.87	6.78	0.4	6.25	6.73
5	4.78	5.57	5.95	6.81	0.5	6.32	6.67
10	4.78	5.71	6.17	6.87	1.0	6.44	6.16
15	4.80	5.76	6.24	6.88	..	...	...
20	4.80	5.81	6.28	6.88	2.0	6.54	5.83
25	4.80	5.84	6.34	6.88	..	...	...
30	4.80	5.88	6.37	6.85	3.0	6.58	5.67
35	4.80	5.91	6.39	6.81	..	...	...
40	4.81	5.93	6.41	6.79	4.0	6.60	5.63
45	4.81	5.93	6.42	6.78	..	...	...
50	4.81	5.95	6.44	6.75	5.0	6.60	5.59

TABLE V

Normal Potassium Halide Solutions added to 50 cc Sol A
(Figures given are pH values at 25°C)

Cc. added	KCl	KBr	KI
0	4.75	4.75	4.75
1	5.39	5.28	5.20
2	5.63	5.45	5.33
3	5.80	5.54	5.44
4	5.87	5.61	5.53
5	5.95	5.67	5.59
10	6.17	5.85	5.79
15	6.24	5.96	5.91
20	6.28	6.01	6.00
25	6.34	6.07	6.05
30	6.37	6.12	6.15
35	6.39	6.15	6.22
40	6.41	6.18	6.27
45	6.42	6.22	6.29
50	6.44	6.22	6.32

TABLE VI

Normal Potassium Chloride added to 50 cc each Sol
(Figures are pH units at 25°C)

Cc added	Sol A	Sol B	Sol C	Sol D	$AlCl_3.6H_2O$*
0	4.75	4.81	5.10	4.39	4.36
1	5.39	4.83	5.39	4.51	4.36
2	5.63	4.85	5.56	4.58	4.37
3	5.80	4.87	5.65	4.59	4.39
4	5.87	4 88	5.71	4.62	4.41
5	5.95	4.89	5.74	4.64	4.43
10	6.17	4.97	5.85	4.72	4.47
15	6.24	5.01	5.91	4.78	4.52
20	6.28	5.02	5.93	4.81	4.54
25	6.34	5.05	5.95	4.82	4.56
30	6.37	5.07	5.96	4.85	4.58
35	6.39	5.08	5.96	4.85	4.60
40	6.41	5.10	5.96	4.88	4.61
45	6.42	5.12	5.96	4.89	4.62
50	6.44	5.14	5.96	4.91	4.62

* 5 g per liter.

These results seem to conflict with results reported in the literature by Thomas and Baldwin[17] and Wilson and Kuan,[21] but it should be noted that in their work, large quantities of solid salt were added (3 gram mols per 100 cc) while here the total quantity added was between 0.001 and 0.05 mols per 100 cc. The work of Wilson and Kuan was repeated by the authors, and it was shown[22] that when dilute solutions are used a single effect is noted, but if solid salt is used, the factor of hydration of the ions of the salt enters and tends to mask the chemical effect. This is confirmed by the work of Harned[23] who found that small quantities (0.01-0.05 M) of sodium chloride increased the dissociation constant of water at 25°C, but in greater concentration than 1 molar with respect to the solution, it decreased the dissociation constant.

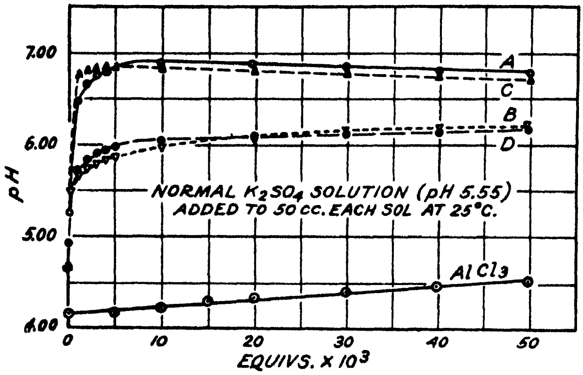

Fig. 4

It will be noted that aluminum chloride solution of the same aluminum content as sol A and C, while showing increased pH values did so to a far less extent than the sols.

Fig. 4 shows that potassium sulfate solution also increased the pH of all sols and reference to Fig. 1 will show that it does so more effectively than potassium chloride solution of same equivalent concentration. Here again it should be noted that the sols A and C acted alike and so did sols B and D.

The authors hope by this time to have shown that one must look for something else to explain the results other than dilution, salt effect on quinhydrone, and hydration of ions. The results with ammonium acetate and potassium oxalate will be even more convincing.

The titration of the sols with ammonium acetate solution is given in Table VIII and in Fig. 5.

The outstanding fact in Fig. 5 is that the effect of acetate ion is ten times greater in increasing the pH of the sols than are nitrate, chloride, and sulfate ions (cf., Fig. 1). It is also shown that the order of reaction was proportional to the aluminum content of the sols (cf., Figs. 3 and 4).

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[21] J. Am. Leather Chem. Assocn., 25, 15 (1930).

[22] Thomas and Whitehead: J. Am. Leather Chem. Assocn., 25, 127 (1930).

[23] J. Am. Chem. Soc., 47, 930 (1925).

It is again emphasized that no maximum was shown by the curves for B and D; that is, the curves approached pH 7 on the vertical axis with increasing salt concentration. But the curves for C and A are parallel to the horizontal axis from 40 to 50, indicating that no change in pH occurred with increase in salt concentration after 40 × 10^2 milli-equivalents were added.

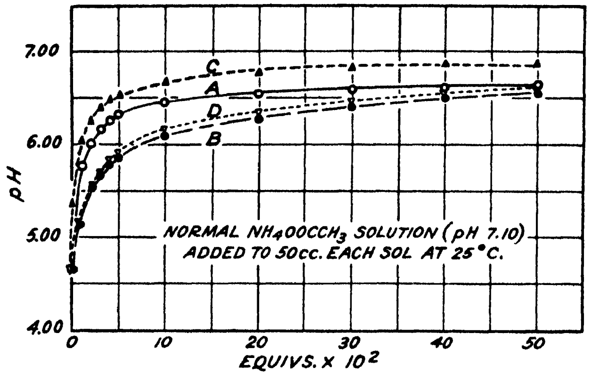

FIG. 5

TABLE VII

Normal Potassium Sulfate Solution added to 50 cc each Sol at 25°C

(Figures are pH values at 25°C)

Cc added	Sol A	Sol B	Sol C	Sol D	$AlCl_3.6H_2O$*
0	4.75	5.42	5.49	4.39	4.14
1	6.47	5.66	6.75	5.73	...
2	6.69	5.75	6.80	5.84	...
3	6.73	5.79	6.81	5.89	...
4	6.78	5.83	6.82	5.94	...
5	6.81	5.86	6.83	5.96	4.16
10	6.87	5.98	6.85	6.03	4.22
15	6.88	6.03	6.82	6.08	4.30
20	6.88	6.07	6.81	6.10	4.35
25	6.88	6.10	6.80	6.10	4.41
30	6.85	6.14	6.78	6.12	4.43
35	6.81	6.17	6.76	6.14	4.44
40	6.79	6.18	6 75	6.15	4.47
45	6.78	6.20	6.73	6.16	4.51
50	6.75	6.22	6.71	6.16	4.53

* 10 g per liter.

Table IX and Fig. 6 reveal the effects of titration of the sols with oxalate. It will be recalled that the oxalate solution consisted of potassium oxalate slightly acidified with oxalic acid.

It will be noticed at once that oxalate ion is very active. The pH of the sols was immediately increased to about pH 7, and except for B, the pH then markedly decreased, gradually approaching the pH of the oxalate solution (5.07). This suggests that a reaction took place with A, C, and D; was completed, and the solution became more acid again. In the case of sol B, the second effect was much less readily executed. This sol contained more aluminum micelle than the others.

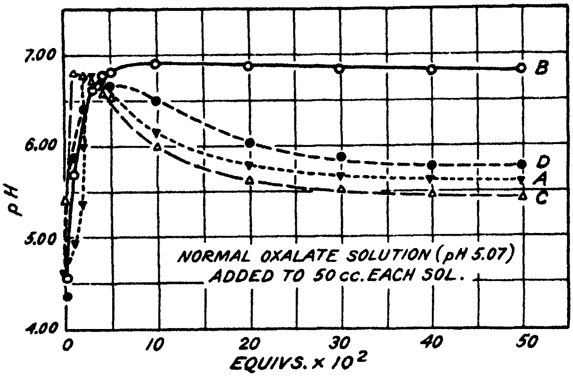

Fig. 6

Table VIII

Normal Ammonium Acetate added to 50 cc of each Sol at 25°C
(Figures are pH values at 25°C)

Cc added	Sol A	Sol B	Sol C	Sol D
0.0	4.75	4.59	5.39	4.39
0.1	5.75	5.18	6.01	5.18
0.2	6.00	5.53	6.25	5.51
0.3	6.19	5.66	6.38	5.69
0.4	6.25	5.78	6.47	5.81
0.5	6.32	5.85	6.54	5.89
1.0	6.44	6.08	6.67	6.14
2.0	6.54	6.29	6.79	6.34
3.0	6.58	6.42	6.85	6.47
4.0	6.60	6.51	6.88	6.58
5.0	6.60	6.56	6.88	6.64

Table IX

Normal Potassium Oxalate Solution added to 50 cc each Sol
(Figures are pH values at 25°C)

Cc added	Sol A	Sol B	Sol C	Sol D
0.0	4.75	4.56	5.41	4.37
0.1	4.99	5.69	6.82	4.88
0.2	5.39	6.39	6.77	6.41
0.3	6.77	6.62	6.71	6.56
0.4	6.73	6.78	6.59	6.64
0.5	6.67	6.82	6.54	6.67
1.0	6.16	6.91	6.00	6.50
2.0	5.83	6.89	5.63	6.03
3.0	5.67	6.85	5.51	5.88
4.0	5.63	6.78	5.46	5.76
5.0	5.59	6.77	5.42	5.76

Resumé of Results between Sols and Salt Solutions

Figure 1 showed the order of the effectiveness of the salt solutions in increasing the pH of sol A to be:

Nitrate < Chloride < Sulfate < Acetate < Oxalate.

Figures 3, 4, 5, and 6, showed all sols acted similarly to sol A, so we can say that the same order would apply to the other sols. Figure 2 showed the similarity of the halogens, so that it may be said that the order of anion effect on pH of positively charged aluminum oxychloride hydrosols is:

Nitrate < Halides < Sulfate < Acetate < Oxalate.

This order was found for aqueous solutions of chromic salts by Gustavson,[4] and by Stiasny[24] for solutions of chromic salts that had previously been heated.

All results showed that sols B and D acted similarly despite the fact that ammonium ion was present in B while absent in D as a result of the initial preparation of the hydrous alumina.

Neutral Salt Titration of Aluminum Chloride Solutions of Different Basicities

After the titrations of the sols with the salt solutions had been completed it was considered advisable to include in this paper a few similar measurements made upon crystalloidal aluminum chloride solutions. Selecting sol D for comparison, a solution of aluminum chloride hexahydrate (5 gm $AlCl_3.6H_6O$ per liter) was made containing the same amount of aluminum as sol D. Then a potentiometric titration of the aluminum chloride solution with 0.1 N NaOH was carried out at 25°C, using the quinhydrone electrode, to determine the exact stoichiometric relation, this was found to agree with the calculated amount, *i.e.*, 30.50 cc of 0.1 N NaOH for 50 cc of aluminum chloride solution. To make the basic solutions, 25 cc portions of aluminum chloride solution (containing 10 grams $AlCl_3.6H_2O$ per liter) were mixed with 10.17 cc and 20.34 cc respectively of 0.1 N NaOH mentioned above and the final volume made up to 50 cc with previously boiled and cooled distilled water. Thus 50 cc portions of $AlCl_3$, $AlOHCl_2$, and $Al(OH)_2Cl$, were obtained all containing the same aluminum content.

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[24] Stiasny and Balanyi: Collegium, 694, 72 (1928).

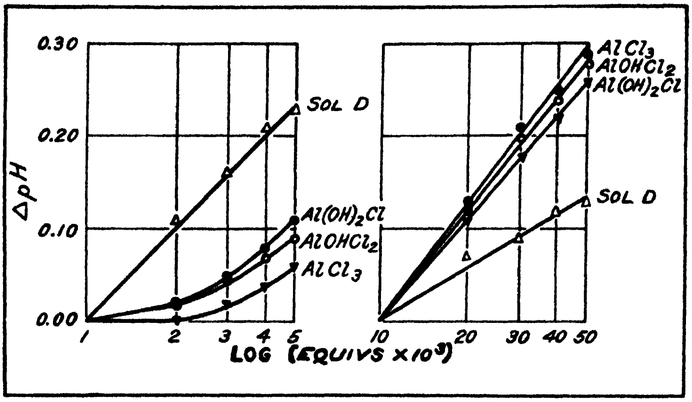

Fig. 7

Each of these portions was then titrated with the same 1 N potassium sulfate solution at 25°C according to the technique previously described.

Table X

Normal Potassium Sulfate Solution added to 50 cc Portions of Each Aluminum Salt Solution at 25°C.

*(Figures are differences in pH units; 25°C)

K_2SO_4	$AlCl_3$		$AlOHCl_2$		$Al(OH)_2Cl$		Sol D	
Cc	pH	ΔpH*	pH	ΔpH*	pH	ΔpH*	pH	ΔpH*
1.0	3.77		3.88		4.14		5.73	
2.0	3.77	0.00	3.90	0.02	4.16	0.02	5.84	0.11
3.0	3.79	0.02	3.93	0.05	4.19	0.05	5.89	0.16
4.0	3.81	0.04	3.95	0.07	4.22	0.08	5.94	0.21
5.0	3.83	0.06	3.97	0.09	4.25	0.11	5.96	0.23
10.0	3.91		4.06		4.34		6.03	
20.0	4.04	0.13	4.19	0.13	4.45	0.11	6.10	0.07
30.0	4.12	0.21	4.26	0.20	4.52	0.18	6.12	0.09
40.0	4.17	0.25	4.30	0.24	4.56	0.22	6.15	0.12
50.0	4.19	0.29	4.39	0.28	4.60	0.26	6.16	0.13

The potentiometer readings were made until constant over a fifteen minute period to plus or minus 0.5 millivolt but are recorded only to the nearest millivolt in Table X. The results are plotted in Fig. 7.

It is evident that potassium sulfate decreased the hydrogen ion activity of all the aluminum solutions and of the sol. It is also seen that the rate of change of pH with respect to change in concentration of K_2SO_4 is not the same in any two cases but is greatest for sol D and least for $AlCl_3$ with the addition of K_2SO_4 solution up to and including 5 cc. The addition of from 10 to 50 cc of K_2SO_4 solution caused a reversal of this order but again there is a progression from sol D through the $Al(OH)_2Cl$ and the $AlOHCl_2$ to the $AlCl_3$ state.

This suggests then that the rate of change of pH with respect to change in concentration of potassium sulfate is a function of the hydroxo groups contained in the basic complex aluminum ion since practically every other condition was held constant. (It should be remarked that the sol was *made up originally* at 70°C, and cooled to 25°C, while the aluminum salt solutions were made and maintained at 25°C, throughout. This was the factor that was not constant in the comparison between sol and solutions and the numerical difference in change of pH with increased concentration of potassium sulfate, although one of degree only, suggests that a closer analogy would have been obtained if this factor, too, were constant.)

Discussion of Results obtained

In attempting to account for the results reported, the same difficulty is encountered that Werner, Pfeiffer, Bjerrum, Gustavson, and Stiasny encountered in working with other complex basic salts; namely, the difficulty of applying the laws of hydrolytic dissociation and the various hypotheses of salt effects.

Hydrolytic equilibria as obtained with simple crystalloidal solutions, such as of potassium cyanide, are not shown by aluminum oxychloride hydrosols. Table III showed that the equilibrium was not immediately disturbed by heat, but on prolonged heating it was disturbed. It likewise showed that upon cooling back, the equilibrium was not shifted back to the original stage.

Tian[19] has suggested that a system like aluminum oxychloride hydrosol may be considered as a heterogeneous system in which the basic salt ion is the dispersed phase. This would explain why upon ageing at 20°C, the hydrogen ion activity increases because the assumption of a dispersed phase introduces a surface phenomenon which would, of course, decrease the original surface exposed by the ions and cause the equilibrium to be disturbed, for example:

$$AlCl_3 + HOH \leftrightarrows AlOHCl_2 + HCl$$

In this case, $AlOHCl_2$ is the supposed dispersed phase, whose formation decreases the surface, and causes a shift in equilibrium to the right; and this results also in hydrogen ion being increased. But if the temperature of such a system should be increased, the degree of dispersity would increase,[25] this would increase the surface and so should shift the equilibrium to the left; *i.e.*, decrease the hydrogen ion activity. Table IV shows that the opposite is true. This was also found to be the case for ferric salts[26] and by Stiasny[27] for chromic salts.

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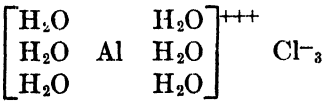
[25] March: Ann. Physik, 84, 605 (1927).

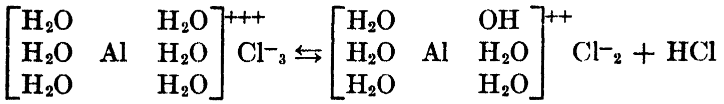
To explain the effect of ageing and heat, then, one must look to some other source. The Werner-Co-ordination Theory[28] offers a consistent explanation for these results.

The aluminum chloride hexahydrate used precipitated three mols of silver chloride per mol of aluminum salt with silver nitrate. Therefore the followng structure can be assigned:—



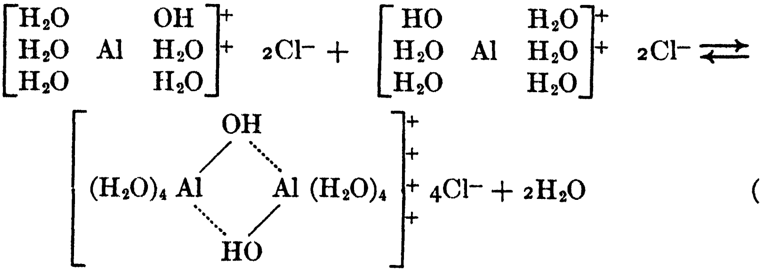
$$\begin{bmatrix} H_2O & & H_2O \\ H_2O & Al & H_2O \\ H_2O & & H_2O \end{bmatrix}^{+++} Cl^-_3$$

Its hydrolysis according to the $CrCl_36H_2O$ analogue is:—



$$\begin{bmatrix} H_2O & & H_2O \\ H_2O & Al & H_2O \\ H_2O & & H_2O \end{bmatrix}^{+++} Cl^-_3 \leftrightarrows \begin{bmatrix} H_2O & & OH \\ H_2O & Al & H_2O \\ H_2O & & H_2O \end{bmatrix}^{++} Cl^-_2 + HCl \qquad (1)$$

To account for lack of mobility in the shift of equilibrium, we can picture the aluminum oxychloride sol as resembling the polyol basic chromic salts reported by Bjerrum.[1] Bjerrum working with chromic sulfate, found that if he heated his salt solutions to boiling that their molecular weights as determined by freezing point method had values around 750. Stiasny[27] working with the same salt, found that heat decreased pH and that on cooling the pH did not return to its original value. Substituting Al for the Cr of Bjerrum's picture, we have:



(2)

In the above picture it is postulated that the hydroxo groups become more firmly bound which diminishes their tendency to unit with H^+ ion to form aquo groups. Thus the tendency for reversal of the hydrolysis equation by heating is lessened.

The authors present the point of view that the colloidal aggregates are formed according to the mechanisms of equations (1) and (2). That is, heating caused two things to take place:

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[26] Thomas and Frieden: J. Am. Chem. Soc., **45**, 22 (1923).
[27] Stiasny and Grimm: Collegium, **694**, 53 (1928).
[28] Thomas: "Inorganic Complex Salts" (1924).

1. Aquo groups gave up hydrogen ions, leaving hydroxo groups in place of aquo groups.

2. The hydroxo groups then "olated," resulting in the formation of large aggregates, eventually reaching colloidal size.

The Werner Theory as extended by Bjerrum and by Stiasny, therefore, offers a consistent explanation for the formation of the sols, for their decrease in acidity upon ageing and increase on heating, for their sluggishness in readjustment of equilibrium, and for effect of heat upon solubility of aluminum hydrates.

The explanation of the results obtained with salt solutions will now be attempted. It is probable that the more aluminum atoms present in the original aluminum chloride solution, the more olated hydroxo groups there were in the sol produced. (Washing removed the hydrochloric acid of hydrolysis.) It would be expected, then, that the greater the degree of olation, the more sluggish would be the reaction of the complex olated ion. Since in every case this complex ion was positively charged, it suggests that not more than two hydroxo groups were present per atom of aluminum. Now when a salt such as potassium sulfate was added to a sol, the hydrogen ion activity decreased, suggesting that sulfate ion was replacing hydroxo groups in the Werner complex. The hydroxo uniting with hydrogen ion to form water would decrease the hydrogen ion activity. Stiasny[3] analyzed basic chromic salt complexes before and after the addition of sulfate solution, and found that sulfate did go to the chromic complex. This is obviously the case with oxalate ion, because the addition of much oxalate changes the chromium from the cation to the anion.[3] This offers a simple explanation for the results shown in Figs. 1 to 4, inclusive.

The anion order, then represents the "penetration power" of the several anions toward the complex basic aluminum ion. On this basis, oxalato complexes are least dissociated, and nitrato complexes most dissociated. Gustavson[4] found this to be true in chrome tanning.

The anion penetration order explains why Lamb[29] got complete precipitation of chloride ions from green $CrCl_3$ with silver acetate, but not with silver nitrate. Some chloride was in the complex with chromium. Nitrate is below chloride in the penetration order, but acetate is above it and the latter then possesses the property of replacing chloride in the "nucleus" forcing it into the "outer solution."

The agreement among the basic aluminum salt solutions (Fig. 7) indicated that their behavior is a function of the hydroxo groups present in the basic aluminum ion and that an aluminum oxychloride sol is a very large basic aluminum ion carrying a positive charge and in equilibrium with chloride ion.

The difference in behavior with respect to small amounts of K_2SO_4, and to larger amounts suggests that hydrolytic dissociation in addition to anion penetration took place at first and when no further hydrolytic dissociation was possible, only the factor of anion penetration was involved. The curves in the first half of the figure are in contrast to the almost perfect straight lines in the second half of the figure and suggest a net effect of two unequal factors while the straight lines suggest only one factor producing a linear relation.

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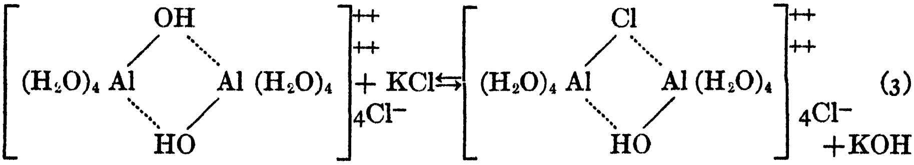
[29] J. Am. Chem. Soc., 28, 1710 (1906).

Using potassium chloride as a typical example to show the anion effect we have:—

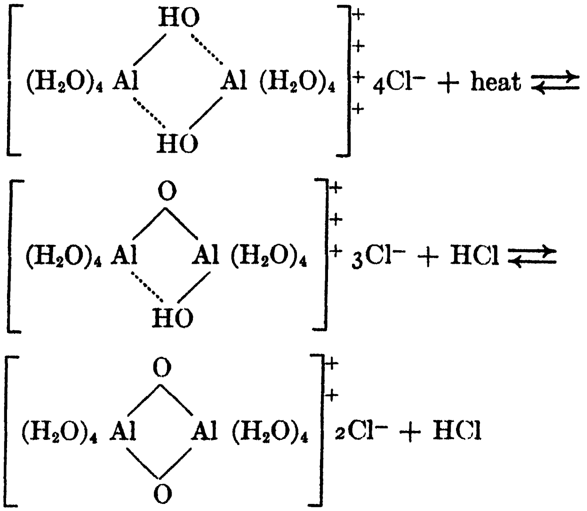


(3)

Since there are many hydroxo groups in a large poly-ol complex ion, the replacement of hydroxo groups will be a function of the concentration of anion added until the maximum penetration for each anion has occurred. This accounts for the maxima in several of salt titration cruves. (Fig. 4, for example.)

On the basis of the evidence submitted the authors present Fig. 8 as representing qualitatively their concept of an aluminum oxychloride hydrosol.

If in Fig. 8 Cr is substituted for Al it becomes the Bjerrum formulation of a poly-ol chromium complex. As stated, this figure is a mere qualitative picture of a simple ol compound since the authors do not know how many aluminum atoms are contained in the colloidal ionic micelle. It is possible. for such an ionic micelle to contain "oxo" groups as well as hydroxo groups. The idea of "oxo-lation" originated by Stiasny is shown in equation (4), which illustrates the conversion of one mole of hypothetical octa-aquo-diol-dialumini tetrachloride to the final product of one mol of the dioxo compound plus two mols of HCl.



(4)

With the conversion of hydroxo groups to ol groups to oxo groups there results increasing resistance to the action of acids. It may be that one of the differences between aluminum oxide hydrosols made by peptization of freshly precipitated hydrous alumina and made by the Crum[30] method of boiling a solution of aluminum acetate is that the latter is more oxolated than the former. The authors hazard the guess that the oxolation of ol complexes would result in a loss of the reaction with neutral salts described in this paper.

It is seen that oxolation results in a diminished charge on the ionic micelle. The Crum aluminum oxide sols are less stable than those made by peptization by acids of freshly precipitated hydrous alumina.

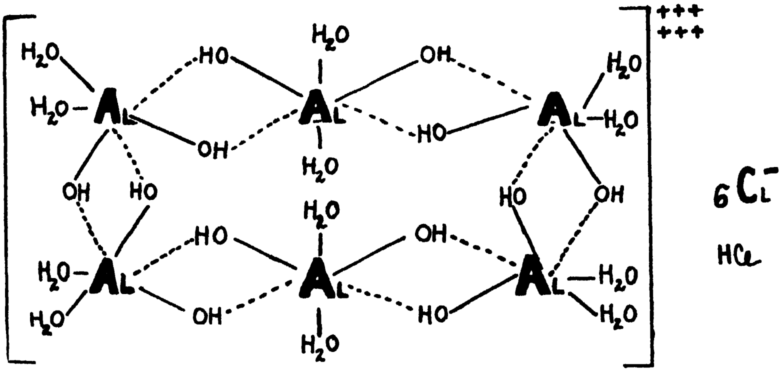


FIG. 8

The ideas submitted by the authors concerning the structure of aluminum oxychloride sols, olation and oxolation were suggested by identical postulates for basic chromium salts made by Bjerrum and by Stiasny and his co-workers.

The postulate that the alkalinity resulting upon the addition of neutral salts is due to replacement of hydroxo (or ol) groups is new in this paper.

The Werner theory with the extensions by Bjerrum and Stiasny so consistently account for the results obtained that the writers believe its application to other similar colloids will be fertile.

Summary

1. Ageing of aluminum oxychloride sols, prepared as described in this paper, at 20°C, resulted in decreased hydrogen ion activity.

2. Heating of such sols resulted in increased hydrogen ion activity and subsequent cooling did not immediately decrease it.

3. The addition of neutral salts to the sols produced a decrease in the hydrogen ion activity.

4. An anion order was established, namely:—oxalate > acetate > sulfate > halides > nitrate which is identical to the "anion penetration" order of Stiasny.

5. Explanations for these results and a suggestion for the constitution of such sols have been offered on the basis of the Werner theory and its extension by Bjerrum and Stiasny.

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[30] Ann. Chim. Phys., (3) **41**, 185 (1854); Ann. Chem., **89**, 156 (1854).

EQUILIBRIUM PHENOMENA IN COAGULATION OF COLLOIDS[1]

BY E. F. BURTON AND MAY ANNETTS

I. Introduction

The study of phenomena observed in the light scattered from liquids has resulted in bringing the technique of these observations into a high state of perfection.[2] As a consequence this method has already been applied by various workers to follow changes taking place during coagulation of colloidal solutions. The original intention in the present experiments was to use the changes in scattered light to follow changes in samples of colloid to which extremely small amounts of various electrolytes had been added. These results led to the complementary experiment of testing the effects of the coagulation process on the light transmitted by a sample of colloid. The latter in turn led to the discovery of the existence of apparently permanent stages of partial coagulation which do not appear to have been accentuated before. The following account consequently consists of four different parts, *viz.*,

1. Light scattered by aqueous sols of gum mastic and arsenious sulphide during coagulation.
2. Energy transmitted by the above sols during coagulation.
3. Stages of partial coagulation of various sols by small traces of electrolytes.
4. Observations on the structure of arsenious sulphide.

II. Light scattered by Sols during Coagulation

Light scattered by a sample of colloid was studied by the use of a pyrex glass cross similar to that used by Martin in the study of pure liquids. The intensity of the scattered light was compared with that of the incident light by the method fully described by Martin and by Sweitzer.[3]

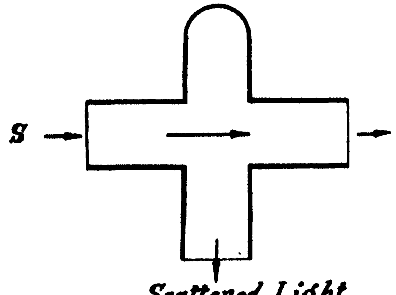

FIG. 1

(i) *Mastic Sol.* This sol was prepared by dissolving gum mastic in absolute alcohol and adding a small quantity of the alcoholic solution to a large amount of water. Small quantities of electrolyte were added to various 100 cc samples and the variation in the intensity of the scattered light was observed. In every case this intensity decreased to a value which remained constant until the particles began to settle visibly. The time required for the intensity to reach this steady value depended on the amount of electrolyte added, but in a curious manner. Table I and Fig. 2 record this action for the salts N/5 aluminium nitrate, N/5 aluminum sulfate and N magnesium sulfate.

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[1] This work was carried out in part with the aid of a Scholarship from the National Research Council of Canada.

[2] Martin: Alexander's "Colloid Chemistry," 1, 340 (1926).

[3] J. Phys. Chem., 31, 1150 (1927).

TABLE I

Cc. of Elect. added to 100 cc Mastic	Time in minutes necessary to reach Steady Value		
	N/5 $Al(NO_3)_3 9H_2O$	N/5 $Al_2(SO_4)_3.8H_2O$	N $MgSO_4.7H_2O$
0.25	53.5		
0.5	20.3		
0.75	14.0		
1.0	8.7	38	
1.5	8.0	22	
2.0	9.3	6	
2.5		8	
3.0	12.0	9	
3.5	18.0	12	36
4.0	23.0	16	24
4.5		21	
5.0	23.7	23	18
5.5		22	
6.0	20.0	18	16
6.5	9.0	11	
7.0	11.0	8	15
7.5		9.5	18
8.0	15.0	13	21
8.5		16	30
9.0	19.0	7	34
9.5	8.0		23
10.0	4.7	4	12
11.0			7
15.0	4.0	4	4

Fig. 2 shews the existence in this case of a curious zonal effect during the process of coagulation, which would be missed entirely by any less sensitive method. At first sight one might think this effect spurious; with the aluminum nitrate curve, the observation was repeated after an interval of some weeks, the two separate observations being indicated by the points distinguished by circles and squares respectively. It is to be noted in addition, that whereas the trivalent ion (Al) gives two maxima and minima, the divalent coagulating ion (Mg) shews only one maximum and minimum. Apparently here we have some antagonizing effect of the positive and negative ions.

(ii) *Arsenious Sulphide.* This sol was prepared by the ordinary method of bubbling hydrogen sulphide gas through a solution of arsenious acid and clearing of excess hydrogen sulfide by extended bubbling of hydrogen gas through the sol. The addition of electrolyte not sufficient to bring about immediate flocculation (about 1 to 5 cc N/1000 aluminum nitrate per 100 cc As_2S_3 sol.) at once caused the particles to scatter much more light—a change of the order of five times the total change recorded in the mastic experiments. After the sudden increase, a further very gradual increase in the intensity of the scattered light continued until the sol was obviously coagulated, at which time the amount of scattered light rapidly decreased. Fig. 3 illustrates this phenomenon. There was no indication of the zonal effect such as given by mastic.

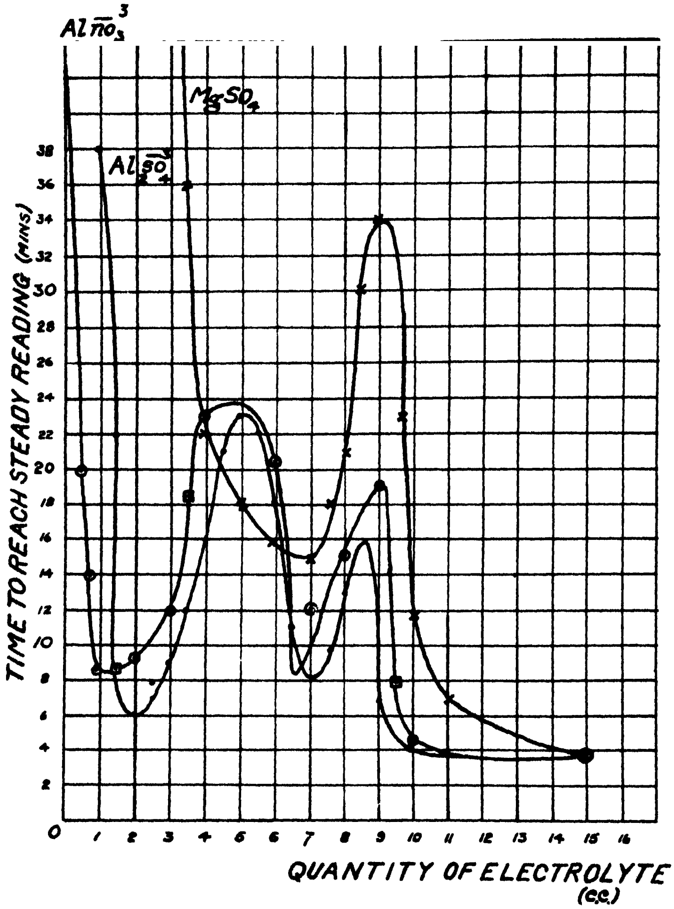

FIG. 2

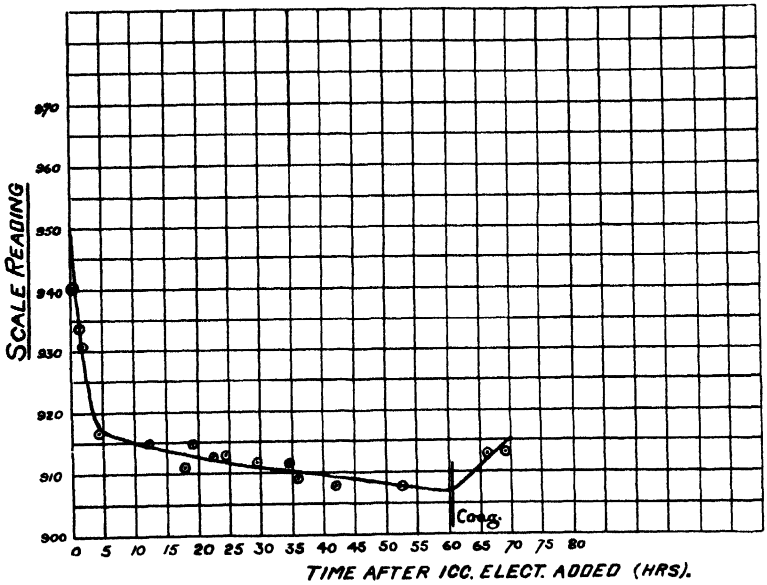

Fig. 3

III. Energy transmitted by Sols during Coagulation

Having made some observations on the scattered light it was natural to follow up with measurements of transmitted energy of radiation on similar sols under similar conditions of coagulation. The simple method of measuring the transmitted energy by means of a sensitive thermocouple was used; the E.M.F. of the thermocouple was measured by a Wolff potentiometer capable of measuring to 0.00001 volt. In essence these measurements are not nearly as sensitive as the measurement of scattered light. The arrangement of

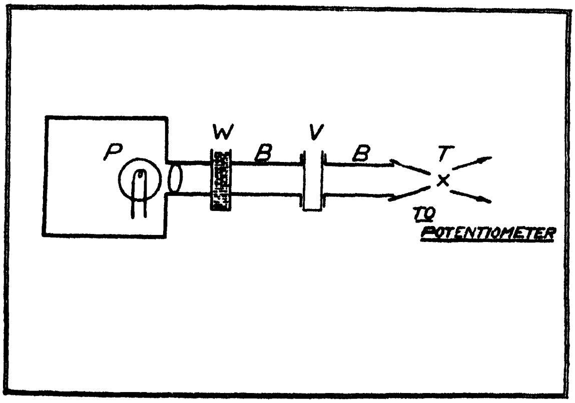

Fig. 4

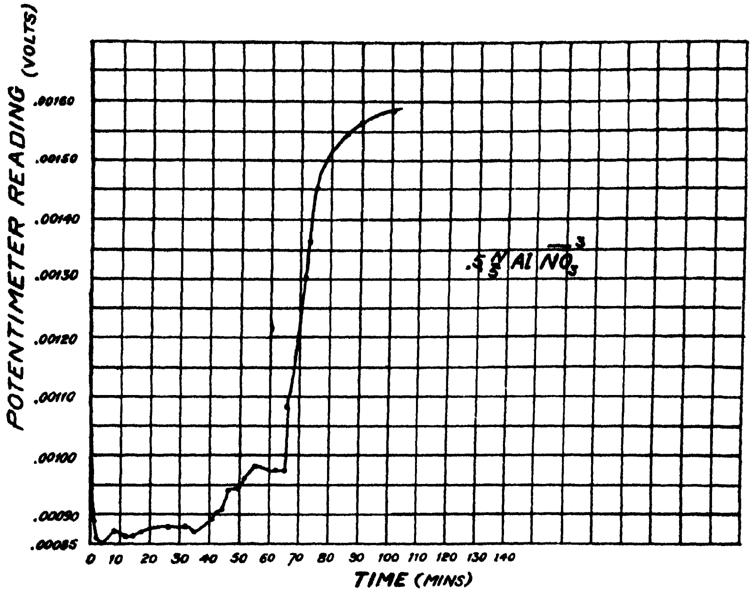
POTENTIMETER READING (VOLTS)
.00160
.00150
.00140
.00130
.00120
.00110
.00100
.00090
.00085
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140
TIME (MINS)
.5 N/5 Al NO3 3

FIG. 5

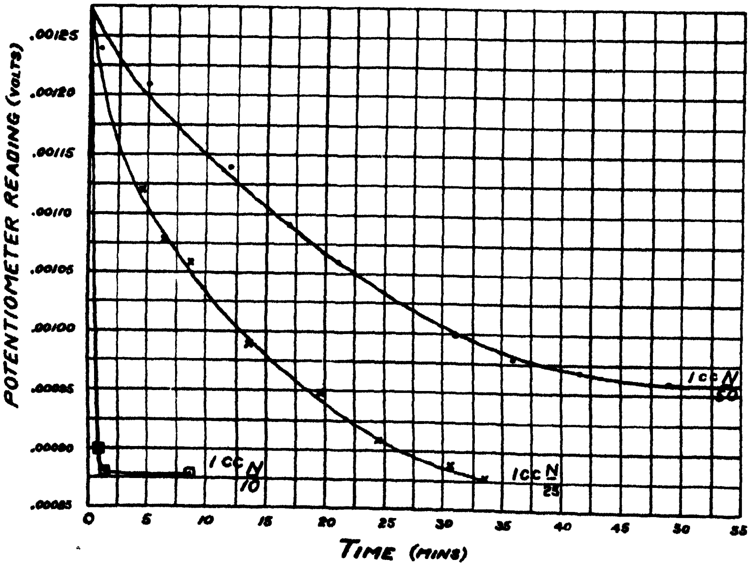
POTENTIOMETER READING (VOLTS)
.00125
.00120
.00115
.00110
.00105
.00100
.00095
.00090
.00085
0 5 10 15 20 25 30 35 40 45 50 55
TIME (MINS)
1cc N/10
1cc N/25
1cc N/50

FIG. 6

apparatus is shewn in Fig. 4, where P indicates a 1000-watt lamp, T the thermocouple, and V the parallel-sided cell of glass containing the sample of sol. B is blackened pipe for protection. W is a water filter to absorb the long heat rays.

A typical set of readings is shewn graphically in Fig. 5, where the thermocouple E.M.F. is plotted against the time elapsed since the addition of the electrolyte. It is apparent that there is a rather sudden drop in the E.M.F. to a minimum in about four minutes, corresponding to a decrease in the transmitted radiation. In the case illustrated, which is the effect of adding 0.5 cc N/5 aluminum nitrate to 70 cc mastic sol, the transmitted radiation then increases rather irregularly until *t* equals 65 min., when a very sudden increase in the transmission takes place showing a clearing of the sol and a return to practically the value of the transmission of pure water.

Further experiments were carried out to learn how the phenomena occurring in the initial period varied as varying amounts of electrolyte were added. The details are given in Table II and illustrated in Fig. 6, where again the E.M.F. of the thermocouple is plotted against the time in minutes.

TABLE II

Elect. in 70 cc sol.	Time after Elect. added (min.)	Pot. reading (volts)	Elect. in 70 cc. sol.	Time after Elect. added (min.)	Pot. reading (volts)
0 1 cc N/10	0 0	0 00129	0 1 cc N/50	0.0	0.00128
	1.0	0 00090		1.0	0.00124
	2.0	0.00088		5.0	0.00121
	4.0	0.00088		12.0	0.00114
	8.5	0.00088		17.0	0.00109
0.1 cc N/25	0 0	0.00127		21.0	0.00106
	2.5	0.00115		31.0	0.00100
	4.5	0.00112		36.0	0.00098
	6.5	0.00108		43.0	0.00097
	8.5	0.00106		48.0	0.00096
	13.5	0.00099		51.0	0.00094
	19.5	0.00095		71.0	0.00092
	24.5	0.00091			
	30.5	0.00089			
	33.5	0.00088			

They shew that with smaller amounts of electrolyte not only is a longer time required to reach the steady reading (at which the colloid remains until settling out commences) but that this steady state is different. With very small quantities of electrolyte, the sol reaches a steady state for which transmission is higher than for larger quantities of electrolyte; from this condition one gets only partial coagulation.

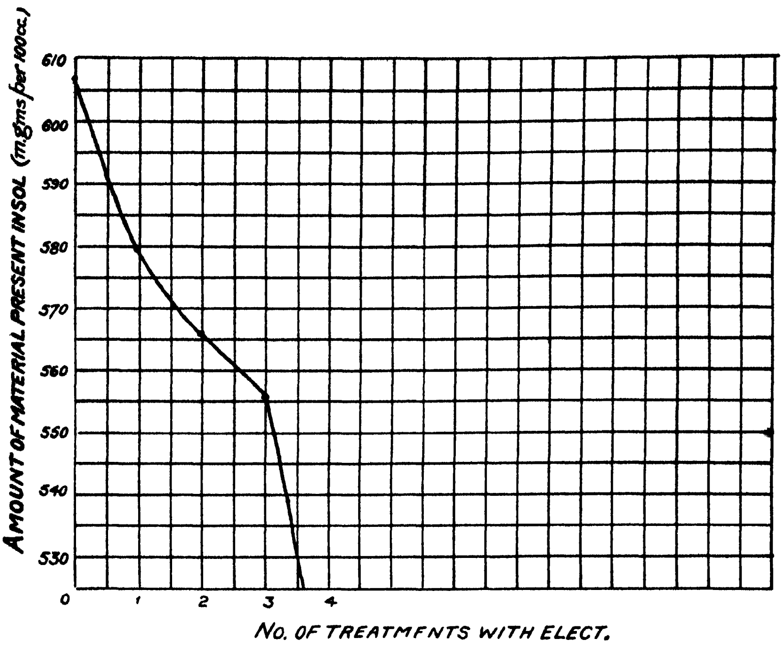
AMOUNT OF MATERIAL PRESENT IN SOL (m.gms per 100cc.)
610
600
590
580
570
560
550
540
530
0
1
2
3
4
NO. OF TREATMENTS WITH ELECT.

FIG. 7

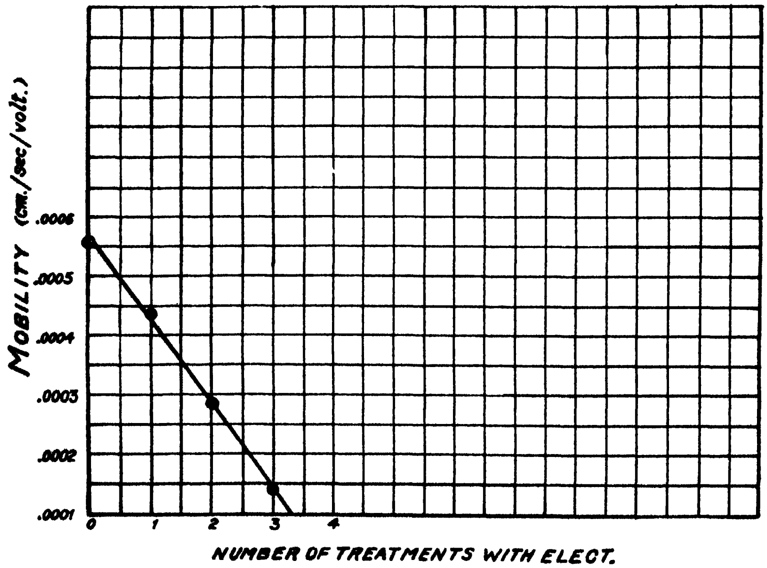
MOBILITY (cm./sec/volt.)
.0006
.0005
.0004
.0003
.0002
.0001
0
1
2
3
4
NUMBER OF TREATMENTS WITH ELECT.

FIG. 8

IV. Coagulation by Stages

During the course of the preceding experiments it was noticed, first with arsenious sulphide, that, when very small traces of electrolyte were added to a given sample of sol, some of the colloidal material was precipitated, but by no means all. Such a state of affairs is suggested, for example, by the curves in Fig. 6. It was thought at first that this partial coagulation might be due to the presence of various sized particles, *i.e.*, that the first amount of electrolyte carried down only the particles above a certain size. But it was found that centrifuging (at 2000 r.p.m.) when continued several hours, so that an appreciable number of particles were thrown out of suspension, did not alter the phenomenon. A series of experiments was carried out with samples of mastic, gold, and arsenious sulfide. To a comparatively large amount of the original sol a small trace of the precipitating electrolyte was added and partial coagulation completed in the course of a few hours; the uncoagulated supernatant portion was drawn off and additional traces of electrolyte added, causing a second partial coagulation. These stages of partial coagulation actually represented states of equilibrium, as such samples shewed no indication of progressive coagulation when kept even for months. In the case of the arsenious sulphide, partial coagulation was repeated until four or five stages were completed. At each stage the concentration of the supernatant sol was measured by weighing the dry residue left after heating samples in an oven at 110° for three hours. Measurements were also made of the cataphoretic mobility of the particles in the sol at each stage. A typical set of results with arsenious sulfide is recorded in Table III and illustrated by the curves in Figs. 7 and 8.

TABLE III

No. of treatments with Elect. (0.1 cc N/100 $Al(NO_3)_3$	Amt. of Material present in sol 100 cc (mgms)	Cataphoretic mobility cm/sec/volt
0	607	0.00056
1	580	0.00044
2	566	0 00029
3	556	0 00014
4	260	
5	0	

The phenomena recorded above afford conclusive evidence that as regards concentration, electric charge, etc., the colloid is in a state of equilibrium with the surrounding medium, particularly in relation to the amount of electrolyte present. The question at once arose as to whether or not the partial coagulation was due to the complete absorption of the precipitating ion by the colloidal material in the precipitated portion. In order to test this, the precipitation was carried out with small quantities of ferric chloride, as iron lends itself to qualitative estimation in very small proportions. The ferric chloride was added and after the partial precipitation was complete, the supernatant colloid was tested for iron, which was found to be present in distinctly definite quantities. The decrease in the cataphoretic mobility of the particles as stage after stage of precipitation occurs shews that the charge on the colloidal particle is reduced step by step as the coagulation proceeds.

V. The Constitution of Arsenious Sulfide Sol

It is generally accepted that the charge on the particles of the sulphide sol is primarily due to the hydrogen sulphide which has been adsorbed by the particles during preparation. The particle may be schematically represented[4] as follows:

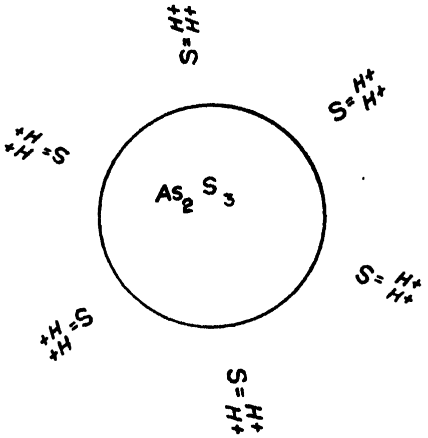

FIG. 9

As pointed out already by Weiser,[5] there is very little to be gained by trying to give a specific formula to any particular sol as the composition varies with preparation, age, etc., We may indicate the composition by the adjustable formula:

$$(nAs_2S_3.mHS)^- + mH^+$$

This suggests that hydrogen sulphide after being intimately adsorbed by the colloidal particle at least partially dissociates leaving the ions HS^- as the charge on the surface if the particle and the H^+ ions as the diffuse outer layer of the Helmholtz double layer.

This theory affords a possible explanation of a strange phenomenon observed during this work. A sample of arsenic trisulphide sol (200 cc) was left standing in a loosely covered graduate. After a few days the upper portion of the sol began to lose its colour dividing the liquid into distinct levels near the top. As time went on the levels gradually merged into one, dividing the liquid very sharply into two sections: the upper one a very pale yellow, almost colourless, the lower one a very dark orange. This level continued to fall with time but no sediment appeared in the bottom of the vessel, and, when viewed both in the microscope and the ultramicroscope a large number of particles could be seen in samples taken from both layers.

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[4] Kruyt: "Colloids," 74.

[5] Weiser: "The Colloidal Salts," 24-25 (1928).

This phenomenon has been repeated with samples of four different arsenic trisulphide solutions including one stabilised by driving off the excess H_2S by bubbling oxygen through. Further it has been shewn that this phenomenon is dependent on exposure to the air, for no settling has been observed in any sample of sol set up in a tube of the same diameter as used above, but having the top sealed off. In one case a sample of sol which had stood two weeks thus without shewing any trace of settling was set up in air in an open tube and shewed a definite settling level in three days. If we suppose that we have complex polysulphide particles in equilibrium with adsorbed ions, ions in the solution, and H_2S, then some of the H_2S will gradually escape to the air, displacing the equilibrium in the direction causing more ions to go into solution and the particles to break down into simple sulphides. Thus arbitrarily designating the particles by $(n\,As_2S_3)mHS^-$ the equations representing the reactions are

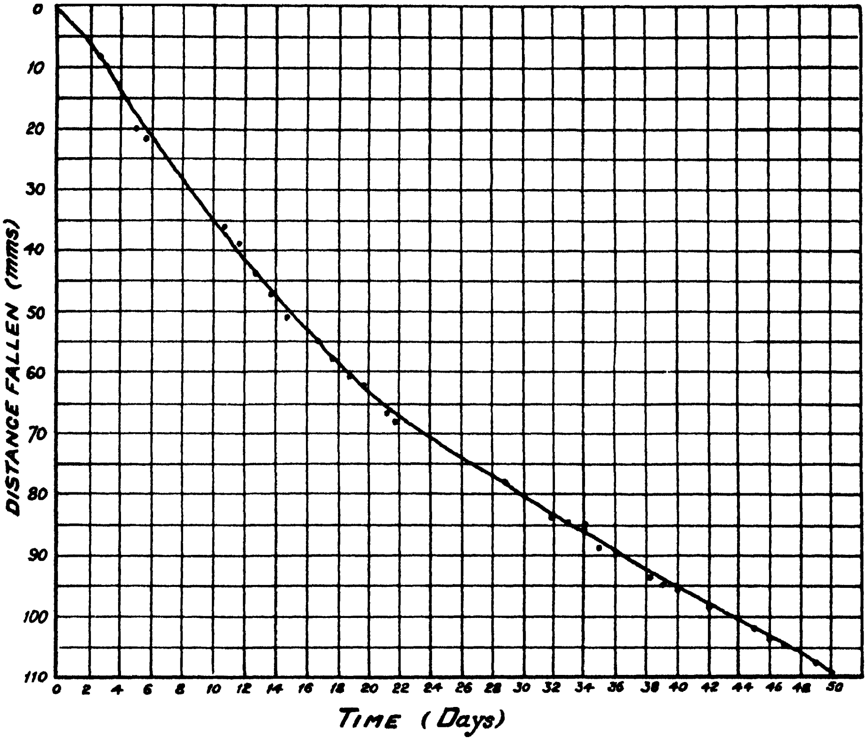

FIG. 10

$$(nAs_2S_3)mHS^- \rightleftharpoons (n\,As_2S_3)\,(m-1)HS^- + HS^- \quad HS^- + H^+ \rightleftharpoons H_2S$$

In the case of coagulation (previously referred to) with ferric chloride, it was found that shortly after coagulation the colloid gave the test for iron in the ferric form, but after a few hours it responded only to the test for the ferrous form. This is in agreement with the above theory of ionisation at the surface of the particle, for in the presence of HS^- ions we would expect the reaction

$$2Fe^{+++} + HS^- \longrightarrow 2Fe^{++} + S_1 + H^+$$

The change of the particles from complex polysulphides to simple sulphides may be regarded as releasing hydrogen sulphide which diffuses up through the solution. The slow fall of the sharp level separating the two layers is determined by the rate of diffusion of gas through the liquid column above.

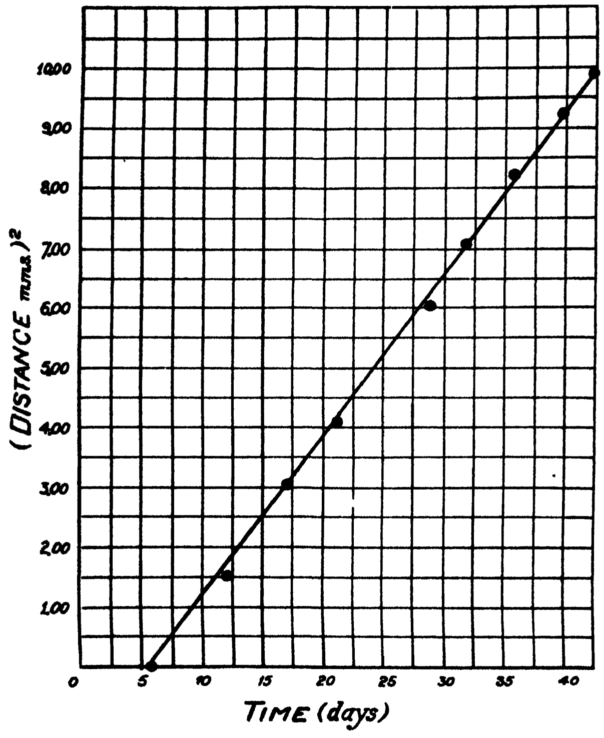

FIG. 11

Suppose the concentration of hydrogen sulphide just at the surface of separation of the two layers is C, and that that at the air-liquid surface is zero. Then if y is the depth of the "pale" layer and D is the diffusion constant, Q the quantity of hydrogen sulphide passing in unit time through unit area perpendicular to the direction of flow, is equal to $\frac{D(C-0)}{y}$ (approx.) so that $Q\,dt = Q\,D\,C/y\,dt$

This hydrogen sulphide must come from the "dark" layer and is the difference between M, the total quantity of material given off in time dt, and the amount used to raise the concentration of this newly formed layer (depth dy) to C.

$$(M-C)dy = D\,C/y\,dt$$

$$y\,dy = \frac{DC}{M - C}\,dt$$

$$t = k_1y^2 + k_2$$

One set of such observations is shewn in Table IV while in Figs. 10 and 11, t has been plotted against y and against y^2. (for nine random values of y and t.)

TABLE IV

Time in days	Distance fallen (mms)	Time in days	Distance fallen (mms)	Time in days	Distance fallen (mms)
3.0	8	17.0	55	36.0	90
3.5	10	18.0	58	38.25	94
4.25	13	19.0	61	39.0	95
5.25	20	20.0	62	40.0	96
6.0	22	21.25	67	42.0	99
11.0	36	22.0	68	45.0	102
12.0	39	29.0	78	46.0	104
13.0	44	32.0	84	47.0	105
14.0	47.5	33.0	85	49.0	108
15.0	51	35.0	89	50.0	110

Summary

1. Experiments have been carried out on the measurement of scattered light and transmitted light from samples of colloidal solutions. These give indication of distinct changes in the colloid on the addition of very small traces of electrolyte even before coagulation sets in.

2. By adding successively very small traces of electrolyte to solutions of gold, mastic, and arsenious sulphide, the existence of stages of partial coagulation has been demonstrated.

3. Suggestions are made as to the constitution of the arsenious sulphide particle.

THE STABILIZATION OF BLUE CUPRIC HYDROXIDE

BY HARVEY A. NEVILLE AND CHARLES T. OSWALD

Introduction

Analyses of the voluminous, gelatinous precipitates which are produced by mixing an alkaline solution with solutions of the salts of iron, chromium, aluminum, and many other metals show a high but variable molecular ratio of water to basic oxide. The water is presumably held by adsorption or loose chemical combination and is gradually lost as the product is dried. The composition of the dried precipitate is thus largely fortuitous and, in general, definite hydrates of the metallic oxides are not formed under such conditions. The so-called hydroxides of these metals are, therefore, more correctly described by the term *hydrous oxides*. In the case of the precipitate formed by the action of an alkali with cupric salts the evidence has been inconclusive and opinion has been divided as to the existence of a definite compound corresponding to the composition $CuO.H_2O$ or $Cu(OH)_2$.

The literature with regard to this question is extensive and has been summarized by Mellor[1] and by Weiser[2]. Both of these authors furnish excellent bibliographies of this subject, so only articles which have a direct bearing upon the present discussion will be listed here.

Many authors refer to the blue precipitate as copper hydroxide while others consider it a finely divided form of hydrous copper oxide which darkens upon dehydration and agglomeration. After reviewing the evidence, Weiser concluded, "The gelatinous body must be looked upon as hydrous cupric oxide rather than hydrous hydrated cupric oxide." The view that blue and black cupric oxides differ principally in particle size is consistent with the general observation that the depth of color of a material decreases with decreasing particle size. It has been stated by some authorities that cupric oxide should be blue since the cupric ion is blue in solution and in most cupric salts, and since this ion and the colorless oxygen ion constitute the cupric oxide crystal lattice. This reasoning is open to criticism since Fajans[3] has clearly shown that the color of an ion depends largely upon the amount of deformation of its electron sheath and that when ions combine to form a crystal the electrons do not remain as they were before combination. For example, he cites the case of yellow lead iodide which is formed from two colorless ions.

The Preparation and Properties of Cupric Hydroxide

The gelatinous blue precipitate obtained by adding a solution of NaOH or KOH in slight excess to a solution of cupric salt will, under ordinary circumstances, quickly turn black. This change in the color of the precipitate will occur while the latter is in contact with the supernatant liquid or while it is being filtered and washed. However, if the precipitation is brought about in dilute solution and at a temperature of about 0°C, the precipitate may be washed with iced water and carefully dried without losing its blue color.

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[1] "Treatise on Inorganic Chemistry," 3, 142 (1923).

[2] "The Hydrous Oxides," (1926).

[3] Physik. Z., 25, 596 (1924).

The freshly made gelatinous precipitate is highly hydrous, containing according to van Bemmelen,[4] more than 20 mols of water to 1 mol of cupric oxide even after pressing between porous earthenware for two hours. This material loses water continuously in a dry atmosphere until its composition corresponds to the monohydrate, $CuO.H_2O$ or $Cu(OH)_2$. This last molecule of water is held rather tenaciously and certain carefully dried or stabilized preparations have been heated to 100°C without further loss in water or change in color.

In addition to the gelatinous form, blue hydrous cupric oxide has also been prepared as a granular or crystalline material by a number of investigators, principally by the action of an alkali on a basic cupric salt. It seems probable, however, that these "crystals" of blue cupric oxide are pseudomorphic transformations of the solid cupric salts. Kohlschütter and Tüscher[5] have shown that transformation products of a given salt crystal retain the shape of the original crystal. This change constitutes what they term a *topochemical* reaction—that is, the replacement of one solid by another.

It is claimed that the crystalline blue monohydrate is more stable than the gelatinous form and the latter is said to change to the crystalline material on standing or under certain treatment. This distinction between the two forms does not seem appropriate since, as our results show, even the highly hydrous blue precipitate is crystalline in nature.

Various substances accelerate and other substances retard the change in color of the gelatinous blue precipitate. The change from blue to black is notably accelerated by small quantities of hydrogen peroxide in alkaline solution. This action is stated by Quartaroli[6] to be still perceptible with 1 part of hydrogen peroxide in 200 million parts of water. Ordinary distilled water contains traces of hydrogen peroxide, formed in the process of distillation, but below the sensitivity of the common reagents for hydrogen peroxide. Such traces are, according to Quartaroli, sufficient to act upon copper hydroxide and cause its alteration or at least accelerate the process. In another article Quartaroli[7] states that copper oxide reacts with hydrogen peroxide to form a suboxide of copper and free oxygen and that the suboxide then reacts with hydrogen peroxide to form the normal oxide. It is interesting to observe how quickly blue copper hydroxide turns black when a solution of hydrogen peroxide is added; at the same time, one may note a marked acceleration of the decomposition of hydrogen peroxide as indicated by the evolution of oxygen.

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[4] Z. anorg. Chem., **5**, 466 (1894).

[5] Z. anorg. Chem., **111**, 193 (1920).

[6] Gazz., **55**, 264 (1925).

[7] Gazz., **54**, 713 (1924).

Weiser[8] found that while dilute solutions of some salts prevent the blackening of the gelatinous blue precipitate, other salts have no effect or accelerate the change. He noticed that those salts which acted as stabilizers have an acidic reaction due to hydrolysis. He first attributed their effect to a slight solvent action on the copper hydroxide converting it into denser clumps which do not change to the black form so readily. The explanation previously offered by Bancroft,[9] that the oxide of the added salt was adsorbed and acted as a protective colloid was discarded because the addition of such hydrous oxides did not result in stabilization and because copper sulfate could be used as the stabilizing salt. As Weiser remarks, "It is inconceivable that the adsorption of blue hydrous cupric oxide should stabilize blue hydrous cupric oxide."

Fowles[10] concludes that the stabilizing effect of such salts as the sulfates of copper, manganese, and chromium results from the removal of adsorbed alkali (an accelerator) and the formation of basic cupric salts which are very stable. He rejects the idea of solvent action since he found that freshly prepared blue cupric hydroxide, when added to a boiling dilute solution of copper sulfate, instantly turned pale green owing to the formation of a basic salt of the reputed composition $3\ Cu(OH)_2.CuSO_4$. On filtering the liquid immediately no copper could be detected in the filtrate by means of potassium ferrocyanide. From this experiment he concludes that no such solvent action as Weiser postulates can possibly occur since after the first second his material was merely heated in water.

Chatterji and Dhar[11] state that blue cupric hydroxide containing a trace of undecomposed copper salt is stabilized by the latter and does not turn black on boiling as would otherwise be the case. With apparent inconsistency, however, they report that the protective adsorbed cupric salt may be washed out by hot water so that the precipitate turns black, but the black product may be rendered blue by boiling it with a solution containing a trace of cupric salt. In testing this statement we have been unable to remove the protective copper salt by means of hot water, but hydrous black cupric oxide is readily converted to a greenish blue product by boiling it with a dilute solution of copper sulfate. It seems clear that we are dealing here with a basic cupric salt. The investigations of Pickering[12] would indicate that a number of basic cupric salts exist in which the oxide or hydroxide is present in a high ratio relative to the anion. He states that when cold dilute sodium hydroxide is added to a solution of copper sulfate, the basic salt, $CuSO_4.3Cu(OH)_2$ is first precipitated and is only slowly converted by dilute alkali to $CuSO_4.9Cu(OH)_2$ and finally to the normal hydroxide. Mehrotra and Dhar[13] have found that all the copper is precipitated from a solution of a cupric salt by less than the equivalent quantity of sodium hydroxide, that either a basic salt is formed or the cupric and sulfate ions are adsorbed in equivalent quantities by the precipitate giving a product of the approximate composition $CuSO_4.3Cu(OH)_2$ or $CuSO_4.6Cu(OH)_2$. It is, therefore, apparent that in order to prepare the blue precipitate free from basic salts or adsorbed copper salts it is necessary to add excess alkali beyond that point at which the supernatant liquid is neutral to litmus or gives no test for the cupric ion.

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[8] J. Phys. Chem., **27**, 501 (1923).
[9] J. Phys. Chem., **18**, 118 (1914).
[10] Chem. News, **128**, 2 (1924).
[11] Chem. News, **121**, 253 (1920).
[12] J. Chem. Soc., **91**, 1982 (1907); **95**, 1417 (1909).
[13] J. Phys. Chem., **33**, 216 (1929).

Effect of Alkalinity.—If an excess of alkali is added to convert the basic cupric salts into the hydroxide, the precipitate quickly turns black, the more rapidly the higher the temperature. As has been indicated above, when less than the equivalent of alkali is added, the precipitate is blue and stable. As shown by the following data, increasing the alkalinity of the solution up to a certain concentration accelerates the blackening of the precipitate but further increase in the alkalinity of the supernatant liquid seems to delay the transformation:

pH of supernatant liquid	color of precipitate
4.57	blue
7.11	blue, black particles
7.28	black
>9.0	dark blue, black particles
>12.0	blue, black particles.

These results were obtained at room temperature by adding various quantities of 2.5 *N* sodium hydroxide solution to separate, 100-cc portions of 0.5 N solution of copper nitrate. All of the precipitates were blue at first and the change from blue to black required some time. The colors indicated above represent the conditions after about 30 minutes and show the relative rates of change.

Preparation at Low Temperature.—Solutions of cupric nitrate (1.0 N) and sodium hydroxide (1.25 N) were cooled to 0°C and equal volumes of the two solutions were mixed in a chilled vessel with thorough stirring. Freshly boiled distilled water which had been cooled almost to 0° was used to wash the precipitate by decantation and on a suction filter until the washings showed no alkalinity to litmus. This precipitate slowly turns black under water at room temperature but remains blue under water if placed in a refrigerator.

Portions of this precipitate which were dried at room temperature in the atmosphere and in a desiccator over sulfuric acid gradually turned black. A portion which was permitted to dry slowly in an electric refrigerator remained light blue and is now stable at room temperature.

Stabilization with Gelatin.—It is apparent that if, in preparing copper hydroxide, sufficient alkali is added to avoid the presence of basic salts, either an inconveniently low temperature must be employed throughout or some stabilizing agent must be used at room temperature. The well-known protective properties of gelatin suggested its use for this purpose.

Equal volumes of solutions of copper nitrate (1.0 N) and sodium hydroxide (1.25 N) were used as in the previous case. Before precipitation a sufficient quantity of 5 per cent gelatin solution was added to the solution of copper nitrate so that the concentration of gelatin was 0.025 per cent by weight of the combined solutions. The precipitate was washed with freshly boiled distilled water by decantation and suction until the washings were neutral to litmus. This precipitate was then dried in an oven at 55°C where it attained a constant weight in 24 hours. Samples of this blue product were powdered and left in the oven at this temperature for a week without any further loss in weight or indication of darkening. This material is rather hygroscopic and absorbs moisture when permitted to cool in contact with the atmosphere.

A sample of the blue powder which had been brought to a constant weight at 55°C was then heated for 20 hours at 105°C. It turned black and lost 16.96 per cent in weight. This sample was then heated over a Bunsen flame and a further loss of 2.95 per cent occurred, making a total loss in weight of 19.91 per cent. The percentage of water by formula in $Cu(OH)_2$ or $CuO.H_2O$ is 18.55 per cent. The loss in weight by our experiments is thus 1.36 per cent greater than the theoretical water content, but this may be accounted for at least in part as due to the decomposition of the adsorbed gelatin at the high temperature and perhaps some reduction of the copper oxide by these decomposition products.

It can be found by calculation that if all the gelatin present in the original solution were adsorbed and carried down by the precipitate, the quantity of gelatin present in the blue product dried to the composition $CuO.H_2O$ would be slightly over one per cent. Determinations by the Kjeldahl method of the nitrogen content of the blue precipitate dried at 55°C and of the original gelatin, dried at the same temperature, show that the quantity of gelatin present in the blue precipitate dried at 55°C is 1.1 per cent. This result shows that, within the experimental error, the gelatin is completely removed from the solution by adsorption on the precipitate.

A sample of this blue product was heated to constant weight at 55°C and was then heated for periods of 24 hours at higher temperatures until the weight was apparently constant at each temperature. As the following data show, a slight additional loss in weight occurred at each temperature up to 95°; above this temperature the loss was much greater:

Temperature °C	Weight of Sample	Per cent Loss	Color of Sample
55	1.9910 g	——	Light blue
65	1.9728	0.92	" "
80	1.9676	1.18	" "
90	1.9622	1.45	Light green
95	1.9498	2.07	Green
105	1.6533	16.96	Black

The nature of the green material obtained at 95°C, as disclosed by X-ray examination, will be referred to later.

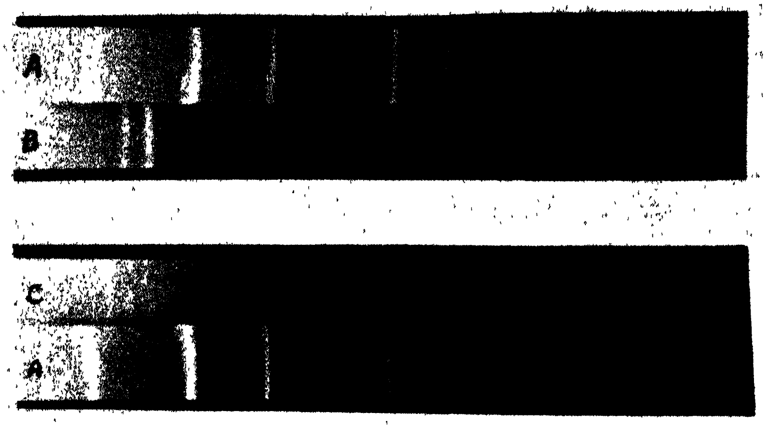


FIG. 1
X-ray diffraction patterns: (A) NaCl; (B) Black CuO; (C) Blue $Cu(OH)_2$.

X-Ray Examination

Materials—Analyses by means of X-rays were made of blue copper hydroxide and black copper oxide to compare them with respect to crystal structure and particle size. The samples used for this purpose were as follows:

1. The blue precipitate prepared at 0° and dried at low temperature as previously described.
2. The blue precipitate obtained at room temperature using 0.025 per cent gelatin and dried at 55°C.
3. The gelatinous blue precipitate prepared as in (2) but used while moist in a cellophane envelope.
4. The black product obtained by heating the dry blue powder at 105°.
5. The black product obtained by heating the blue powder over a Bunsen flame.

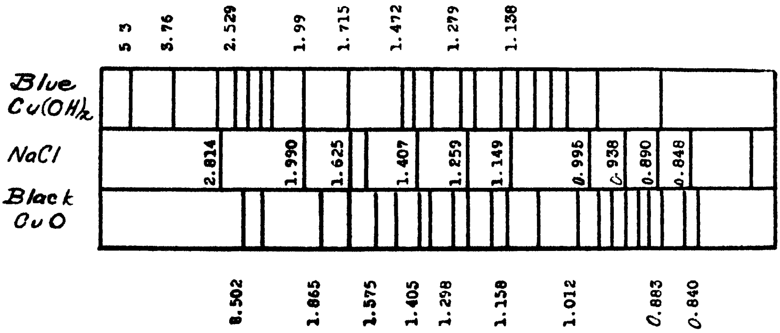


FIG. 2
Inter-planar spacings in Ångström units of the crystals of blue $Cu(OH)_2$, NaCl and black CuO.

6. The hydrous black precipitate obtained at room temperature and used while moist in a cellophane envelope.

7. The green powder obtained by heating the blue material at 95°C as described above.

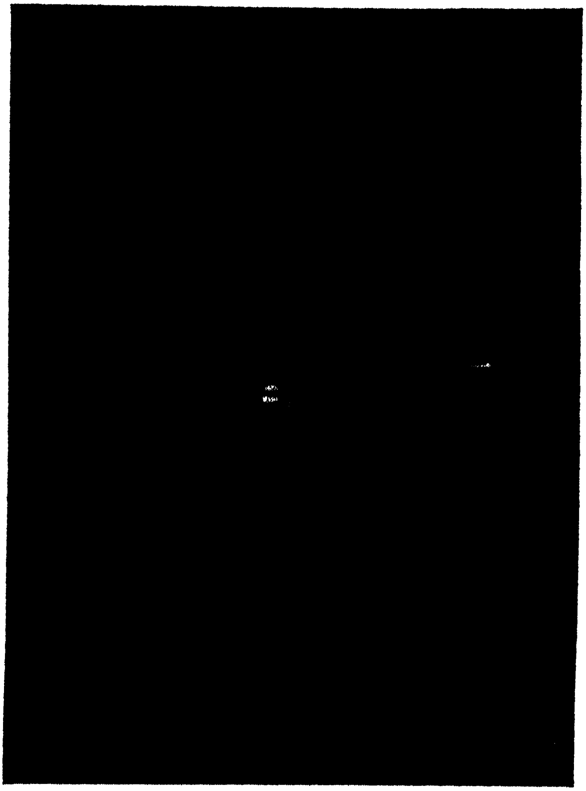


FIG. 3
Monochromatic pin-hole diffraction pattern of black CuO.

Apparatus and Technique—The X-ray outfit used was the General Electric crystal diffraction unit. A Coolidge X-ray tube, operating at 21 milliamperes and 30,000 volts, was employed with a filter which furnished monochromatic molybdenum X-rays ($\lambda_{K\alpha} = 0.712\text{Å}$.)

X-ray diffraction patterns were obtained by two methods: A. The Hull-Debye-Scherrer powder method, using a quadrant cassette. The distance from specimen to plate was 8 inches and the time of exposure was 66 hours; B. The monochromatic pin-hole method with the specimen contained in a cellophane envelope. The distance from specimen to plate was 11 cm and the time of exposure was 66 hours.

Results—Specimens 1 and 2 by method A and specimens 1, 2, and 3 by method B give identical diffraction patterns. Specimens 4 and 5 by method

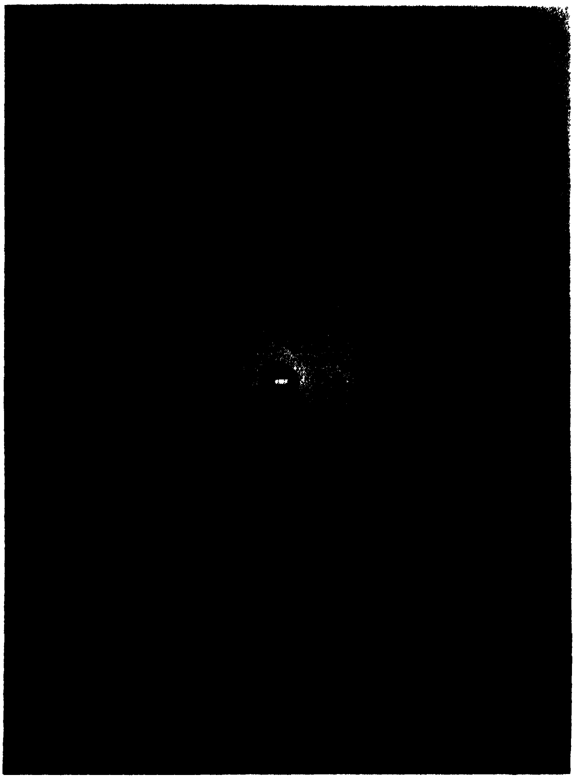
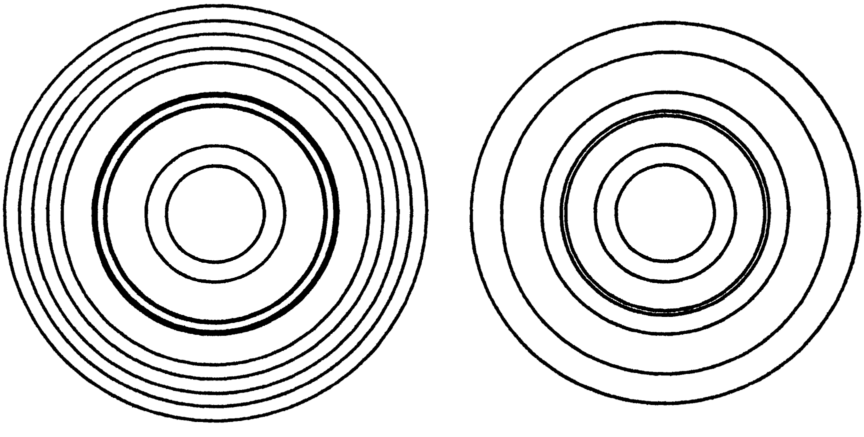


FIG. 4
Monochromatic pin-hole diffraction pattern of blue $Cu(OH)_2$.



Black CuO

Blue $Cu(OH)_2$

FIG. 5
Pin-hole diffraction patterns of black CuO and blue $Cu(OH)_2$.

A and specimens 4, 5, and 6 by method B give the same pattern which is, however, quite different from the pattern given by the blue specimens 1, 2, and 3. The comparison of these two patterns by method A is shown in Fig. 1 and is more clearly demonstrated in Fig. 2 which was drawn from the negatives of the strip films. The interplanar distances recorded in Ångstrom units in Fig. 2 were likewise measured on these negatives. The comparison by method B of the blue and black forms is shown in Figs. 3 and 4 and the contrast is again more clearly brought out in Fig. 5 which was drawn to scale from these photographs.

Specimen 7 when X-rayed by method A gave a pattern which contained the lines corresponding to both the blue and the black substances, and the green material is therefore a mixture of blue copper hydroxide and black copper oxide resulting from a partial decomposition of the former.

Discussion

The X-ray evidence just presented indicates that the blue and the black substances have a distinctly different crystal structure and hence the blue substance is not simply hydrous cupric oxide in finely divided form but is a definite chemical compound, either $Cu(OH)_2$ or $CuO.H_2O$. In this respect our results agree with those of Posnjak,[14] as yet unpublished, but of which he provides the following abstract: "By means of the X-ray powder method the existence of a definite hydrated cupric oxide has been established. Its composition is that of a monohydrate. The blue gelatinous precipitate usually obtained is crystalline, and is identical with the microscopically crystalline preparations. The optical properties of the latter have been determined. It is erroneous to regard the effect of alkalies and various salts on the stability of the gelatinous hydrated cupric oxide as colloidal phenomena, as the changes brought about by such additions are due to interaction accompanied by the formation of some other substance."

In our experiments it was observed in all cases that the diffraction bands or rings obtained by X-raying blue copper hydroxide were much more diffuse than those from the black oxide. This indicates that the ultimate particles of the blue material are much smaller than those of black copper oxide, regardless of whether the comparison is made with the dry powders or with the hydrous precipitates. It would seem then that three factors may be involved in the transformation of the blue gelatinous precipitate to the black oxide. These factors are:

1. Change in chemical composition involving the release of a molecule of water.
2. Change in crystal structure.
3. Increase in the size of the primary particles.

With regard to the first factor, the loss of water by the blue substance does not appear to be a matter of simple dissociation of a hydrate and we therefore conclude that the molecule has the constitution $Cu(OH)_2$ rather than $CuO.H_2O$ Bancroft[15] has pointed out that if a definite hydrate of the composition $CuO.H_2O$ exists with a practically zero vapor pressure it should form from cupric oxide in the presence of water, but the reverse process actually takes place. We have noticed that this change in the color of the precipitate from blue to black in contact with its mother liquor, or under water after thorough washing, or when filtered but still moist, begins at certain nuclei and spreads in all directions. That is, black particles appear at first in the blue mass and these gradually enlarge until the entire precipitate is black. Even the insoluble particles, presumably copper oxide, which may be observed in a solution of commercial copper nitrate will act as centers for this transformation. This difficulty may be avoided by filtering the solution of the copper salt before the precipitation is made. The effect just noted is an illustration of a reaction occurring at the interface between two solid phases, in this case the phases are copper oxide and copper hydroxide. This is a very general phenomenon and has been observed, for example, by Pease and Taylor[16] in the reduction of copper oxide to copper by means of hydrogen and by Jones and Taylor[17] in the same reduction brought about by carbon monoxide.

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[14] Reported at the 78th meeting of the American Chemical Society, Minneapolis, Minn., Sept., 1929.

Kohlschütter and Tüscher[5] have likewise expressed the view that the blue compound is copper hydroxide and that its change to the black oxide is not simply a molecular splitting off of water but involves the internal neutralization of the ions resulting from the amphoteric dissociation of copper hydroxide. The mechanism is illustrated as follows:

$$Cu^{++} + 2\,OH^- \rightleftarrows Cu(OH)_2 \rightleftarrows CuO^{=}_2 + 2H^+$$

$$2\,H^+ + 2\,OH^- \longrightarrow 2\,H_2O$$

$$Cu^{++} + CuO^{=}_2 \longrightarrow 2\,CuO.$$

They maintain that this inner neutralization takes place between molecular complexes of colloidal dimensions and that a definite degree of dispersity is required to facilitate this change. Very high or very low dispersity represses the reaction; between these extremes the stability decreases with increasing dispersion. Equal primary particles may build up larger individuals of looser or more compact structure, the former favoring dehydration and the latter opposing it. If this be the true mechanism of the darkening of blue copper hydroxide, the stabilizing action of gelatin and of low temperature may be understood as inhibiting the agglomeration of the primary particles as they change while drying into a more compact and stable structure. It is well known that gelatin exhibits such protective action both in preventing the agglomeration of fine particles and in interfering with crystal growth.

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[15] "Applied Colloid Chemistry," 246 (1921).

[16] J. Am. Chem. Soc., **43**, 2179 (1921).

[17] J. Phys. Chem., **27**, 623 (1923).

The properties of copper hydroxide are reported by Müller[18] in a series of papers in which he demonstrates its amphoteric nature. He states that $Cu(OH)_2$ dissolves in solutions of NaOH stronger than 12 M, that its solubility is considerably greater than that of CuO in concentrated alkaline solutions, and that the solubility is due to the formation of the cuprate ion rather than to colloidal phenomena. He prepared by crystallization from alkaline solution a cuprate of the probable formula Na_2CuO_2 which was cobalt-blue in color. Müller states that the dehydration of $Cu(OH)_2$ takes place gradually but the product is not water-free CuO.

Creighton[19] has also studied the solutions of copper hydroxide and copper oxide in concentrated alkalies and states that these solutions do not exhibit characteristic colloidal properties. He presents evidence to show that their blue color is due to the cuprate anion.

Further evidence that blue cupric hydroxide is distinctly different from cupric oxide was obtained by Veil[20] who found that the blue compound has a molecular coefficient of magnetization which is approximately three times as great as that of brown or black cupric oxide.

The conclusion that the blue compound is copper hydroxide and not finely divided copper oxide admittedly does not explain the results of Schenck[21] who found that the hydroxides of copper and aluminum when coprecipitated could be heated in the blast lamp without blackening, provided the ratio of copper oxide in the mixture did not exceed 5 per cent. His analysis of the product which remained blue after ignition showed that no water was present so the blue substance in that case was not copper hydroxide. He argues that the blue substance is not an aluminate of copper but concludes that it is finely divided copper oxide stabilized against agglomeration by means of the alumina. Our results do not deny the possibility that cupric oxide may be blue if sufficiently dispersed; in fact they indicate that increase in particle size is one of the factors involved in the color change. It would seem that X-ray analysis might provide decisive evidence as to the nature of the product obtained by Schenck.

Colloidal Copper Hydroxide

In precipitating copper hydroxide in the presence of a considerable quantity of gelatin and with an excess of alkali, it was noted that the supernatant liquid possessed a purple tint. The depth of color of this solution increases with increasing concentration of gelatin or of alkali. These solutions after filtering were examined in the ultra-microscope and the presence of colloidal particles was evident.

Similar sols were also produced by the peptizing action of gelatin and excess alkali upon the blue precipitate, upon hydrous black copper oxide and even by permitting a solution of gelatin (for example, 1 per cent) in dilute sodium hydroxide to stand in contact with commercial copper oxide. In every case it was necessary to have present both gelatin and excess alkali in order to obtain peptization.

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[18] Z. angew Chem., **33**, 303 (1920); **34**, 371 (1921); Z. physik. Chem., **105**, 73 (1923).

[19] J. Am. Chem. Soc., **45**, 1237 (1923).

[20] Compt. rend., **178**, 329 (1924).

[21] J. Phys. Chem., **23**, 283 (1919).

A sample of the purple sol was placed in a collodion membrane and dialyzed against distilled water. The sol was first partially neutralized with hydrochloric acid to prevent the alkali from damaging the membrane. The presence of the chloride ions also furnished a convenient means of testing the rate of dialysis. Tests with silver nitrate showed that practically all of the sodium chloride had diffused through the membrane at the end of 15 hours. The distilled water was changed daily and at the end of 4 days a blue precipitate of copper hydroxide appeared in the dialyzate. This precipitate when dried remained light blue but was horny in nature due to the large proportion of gelatin present. This experiment confirms the observation that gelatin alone is unable to peptize copper hydroxide; when the alkali is sufficiently removed by dialysis the copper hydroxide precipitates.

When an acid is added gradually to the purple sol, copper hydroxide first precipitates at the neutral point and this precipitate dissolves as more acid is added. Sols of copper hydroxide or copper oxide in alkaline solution are negatively charged and the peptizing ion is either the hydroxyl ion or possibly the cuprate ion; gelatin in alkaline solution is also negatively charged so that its efficient aid in forming these sols may be understood. Judging by the depth of color produced in the supernatant liquid, powdered cupric oxide is much more readily peptized in a normal solution of sodium hydroxide containing 1 per cent of gelatin than it is in normal sodium hydroxide containing 5 per cent of glycerol, while a 5 per cent solution of sucrose in normal alkali produces only a faint blue tint after a week in contact with copper oxide. The reddish-purple sols produced with gelatin are quite distinct in color from the familiar blue sols in which copper hydroxide is peptized in alkaline solution with the aid of sugars, glycerol, etc. These latter usually show a precipitation of cuprous oxide on standing, whereas the sols containing gelatin appear to be more stable.

Summary

The blue gelatinous precipitate obtained by the action of an alkali with a cupric salt is variously described as cupric hydroxide and hydrous cupric oxide. The literature relative to the preparation and properties of this substance is reviewed with particular reference to the conditions which retard or accelerate its change to black cupric oxide.

It is shown that the blue compound may be stabilized by precipitating it in the presence of gelatin which is completely removed from solution by adsorption on the precipitate.

By means of X-ray diffraction patterns the blue preparations, both moist and dry, are shown to have a distinct crystal structure which differs from

that of black copper oxide. From this and other evidence it is concluded that the blue substance is cupric hydroxide rather than hydrous cupric oxide.

The ultimate particle size of the blue hydroxide is shown to be smaller than that of the black oxide, and the factors involved in the transformation of hydroxide to oxide are discussed.

A colloidal solution of copper hydroxide peptized by the combined effect of alkali and gelatin is described.

Acknowledgment

The writers are grateful to Professor H. V. Anderson of this university for his valuable assistance in the X-ray analyses described in this paper.

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TRANSMITTED STRUCTURAL BLUE IN MICROSCOPIC OBJECTS

BY CLYDE W. MASON

In the microscopical examination of precipitates, emulsions, sublimates, and other finely divided material, which is known to be colorless, a distinct blue transmission color is sometimes encountered. Although this phenomenon is obviously a case of structural color, it has apparently been noted by few observers, and the conditions governing its appearance have not been formulated. The recognition of the nature of such anomalous color, when it occurs, is of interest in chemical microscopy, and the realization that it may exist should serve as a caution whenever the color of fine structures is studied.

The conditions under which structural transmitted blue is observable are as follows:

1. A fine structure substantially in one plane and possessing uniform dimensions must exist. It may consist of particles distributed irregularly but all of substantially equal diameters, such as may be produced when solids or liquids (silver chloride, sulphur, organic bases) are precipitated from solution, or sublimates (sulphur, arsenic trioxide) are collected on a cool surface. As a simpler case, the structure may be made up of more or less parallel and evenly spaced striations, such as are found on butterfly scales or diatoms.
2. The boundaries of the structural details (particles or striations) must make a "contrasty" image in the microscope. Dry mounted structures, in the form of spherical particles, and deeply incised grooves or ridges in very high relief give the strongest blues.
3. Substantially axial or only slightly convergent brightfield illumination is necessary. The aperture of the illuminating cone should be markedly less than that of the objective. This would ordinarily be the case when the iris diaphragm of the substage condenser is closed as far as possible; opening the diaphragm, so as to flood the object with convergent light, destroys the color.
4. The aperture of the microscope objective must not be too great. The blue color is exhibited best with an objective of aperture barely sufficient to resolve the structure. A given structure may therefore appear blue with a low power objective and colorless with a higher power.

It is evident that the above conditions of microscopical observation are far from impossible of occurrence in ordinary studies.

General Phenomena of Diffraction

The explanation of the origin of transmitted blue must lie in diffraction, for the color disappears in uniform light, as no other type of structural color does, and requires substantially uni-directional light for its observation. Let us consider the diffraction phenomena exhibited by structures of varying fineness.

When a fine structure is illuminated by a narrow pencil of light, secondary radiation is set up from each point on its bounding surface. If the structure is approximately spherical or has some other systematic arrangement of surfaces the diffracted radiations will tend to reinforce each other in certain directions depending on the dimensions and the wave length. With multiple structures, such as particles of uniform size or gratings, these diffraction effects are proportionately enhanced. The minimum dimension which will produce diffraction maxima in a definite direction is equal to the wave length of the light used; the diffracted light is then emitted perpendicular to the illuminating beam. With coarser structures the angle of diffraction is less than 90°.

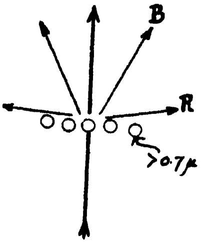

FIG. 1

Diffraction of light by uniformly sized particles, resolvable with all wave lengths of light. Transmitted blue if the aperture of the objective is reduced.

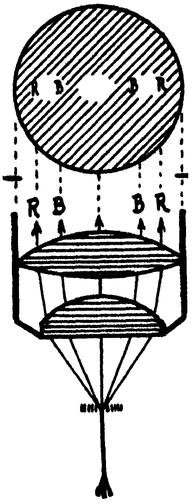

FIG. 2

Diffraction spectra from a grating, as seen at the back aperture of the objective.

So with a 0.75 μ structure, illuminated with white light, red light ($\lambda = 0.75\mu$) will be diffracted at an angle of 90° from the direct beam. The shorter wave lengths will be diffracted at less angles. For a structure of dimensions d the angle α between the diffracted ray and the axis of the illuminating beam is given by $\sin \alpha = \lambda/(n \cdot d)$. The structure will be at the limit of the resolving power of the microscope using axial red illumination, and will be well within the limit for blue light. When a grating (14,000 lines per inch) or As_2O_3 sublimed on a slide is illuminated with a substage condenser diaphragmed as much as possible, and an objective of 0.6-0.9 N. A. is focussed on the preparation, the diffracted rays are clearly visible at the back aperture of the objective when the eyepiece is removed. The axial (unidiffracted) maximum appears as a bright spot of light in the center of the aperture. If the structure is a grating, diffraction spectra are seen on either side of the central beam, transverse of the rulings. If the structure consists of fine uniformly sized particles, these spectra exist as concentric zones of color, the blue end being innermost and the red nearer the periphery of the objective opening. The numerical aperture of the objective required to resolve such structures with axial illumination is given by the formula N. A. $= \lambda/d$.

If the structure is distinctly smaller than the wave length of red light, resolution with all wave lengths is impossible if axial illumination is used. For example, structures having dimensions of 0.4 μ are only barely resolvable with blue light ($\lambda = 0.4^{+}\mu$), the diffracted rays making an angle of nearly 180° with each other. With red light and structures of this size, lateral diffraction maxima are impossible, because light emanating from two points λ apart will be out of phase in any direction except forward along the axis of the beam. As a consequence the structure will tend to transmit preferentially the longer wave lengths, when illuminated with white light.

The diffraction of the shorter wave lengths laterally, out of the path of the direct beam, also follows from the fact that secondary radiations emanating from two points λ apart will be in phase along a direction perpendicular to the axis of illumination. This agrees with the well-known behavior of Tyndall blue media, which ideally have as their maximum particle size about $0.4^{+}\mu$. Still smaller particles will tend to scatter blue more strongly than red, in accordance with Rayleigh's calculations, the intensity being inversely as λ^4.

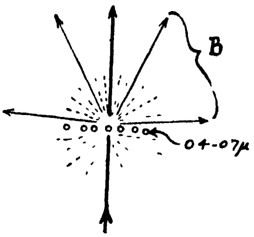

FIG. 3
Diffraction of blue light by particles not resolvable with red axial light. Transmitted blue; longer wave lengths scattered.

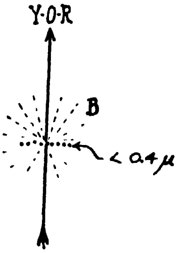

FIG. 4
Scattering of light by particles not resolvable with blue axial light. Tyndall blue scattered; longer wave lengths transmitted.

A single isolated particle (ZnO pigment) of diameter less than 0.4μ can be seen to scatter a clear blue light when illuminated orthogonally in a slit ultramicroscope; such particles are deep orange by transmitted light. Similar phenomena are observable with aggregates of fine needle-like crystals as well as in the case of numerous other examples of Tyndall blue. The scattered blues are better if the particles are in a thin layer, and the red or orange transmission color is stronger the thicker the layer of particles traversed. In general, smaller particles give a deeper blue, and the blues become paler and whitish if the particles grow larger.

In connection with the scattering of blue and the transmission of red by structures 0.4μ or smaller, it is of interest to consider how coarser structures may effect light of longer wave length. By using red light (0.75μ) and a 0.7μ structure, the system is in effect almost doubled in scale. Laterally diffracted radiations will be in phase, and therefore red light will tend to be scattered. Blue light will be diffracted at a lesser angle, and hence will travel in a general forward direction through the system. In general, since the longer wave lengths are diffracted more than the shorter ones, there will be a tendency for red to be deviated out of the path of the illumination beam, and for blue to pass through the system more nearly parallel to this path.

In addition to the above points regarding diffraction, which are also the basis of Abbe's theory of microscopic resolution, the character of the diffracting structure is of great importance in the production of the various color phenomena. The intensity of the diffracted light depends to a large extent on whether the refractive indices of the structure and its surrounding medium are markedly different or nearly identical. In the latter case a large proportion of the light passes through the system without diffraction, and if the illumination is white, simply serves to mask the effect of removal of certain wave lengths by deviation from the direct beam. The brilliancy of the diffraction spectra and of the scattered light is very greatly reduced under these conditions.

The shape of the diffracting structure likewise governs its effects. A grating having faint or shallow rulings (as most artificial gratings do) will allow a large proportion of the light to pass through it undiffracted, and will yield relatively faint colors. Wood[1] emphasizes the importance of the depth of the rulings in intensifying the brilliancy of the diffracted light at the expense of that directly transmitted.

Experiments with Microscopical Structures

In applying the principles of diffraction to explain the colors of microscopic objects, it is to be expected that such boldly contoured objects as fine particles of solids or liquids, perforated or embossed diatom valves, or deeply grooved butterfly scales, will show more striking color effects than can be expected from artificial gratings. Such objects, when mounted dry, exhibit relatively strong diffraction which may be related to their color phenomena by rather simple experiments.

A "natural diffraction grating" may be taken as the first and least complicated case.

The unpigmented scales of the common "Silverspot" (*Argynnis*) butterfly are deeply striated, and under ordinary conditions appear colorless. Under the microscope with a 5.4 mm, 0.74 N. A. objective the striae are easily resolved. The image is black and white with axial illumination. At the back aperture of the objective two orders of diffraction spectra are brilliantly visible on either side of the colorless axial beam from the diaphragm opening of the condenser. These spectra are crosswise of the striae, with their red ends outermost. The purity of the spectra is greatly enhanced by narrowing the illuminating beam, and they are lost due to overlapping when the condenser is increased.

On reducing the aperture of the objective, by means of an iris diaphragm near its back focal plane, to about N. A. 0.50, only one pair of spectra (first order) is included by the objective. The image is black and white and the striae are easily resolved. Further reduction of the aperture produces a succession of colors in the image: yellow green, blue green, blue, and violet. Correspondingly, the red, orange, and yellow portions of the diffraction spectra are cut off by the diaphragm. When the objective is diaphragmed to N. A. 0.25, the structure is barely resolvable and is a strong blue by transmitted light. At the back aperture of the objective only the white axial beam and the intense blue inner portions of the two diffracted spectra are visible. The structure is not resolvable by red light, with this numerical aperture.

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[1] "Physical Optics," 219 (1919).

If the opening of the objective is reduced below 0.25 N. A. the structure is not resolvable even with blue light, and its transmission color goes from blue or violet to dark brownish orange or yellow. No diffraction spectra are visible at the back of the objective.

On rendering the illumination slightly oblique instead of axial, by displacing the condenser diaphragm laterally of the striations, the transmitted blue is perfectly restored, together with the resolution, and correspondingly the blue end of one of the diffracted spectra is seen to enter the aperture of the objective.

The dark-brownish transmission color, observed when the objective is diaphragmed so that no part of the diffraction spectra is included by its aperture, is due to the fact that there is some scattering of light in addition to the diffraction in definite maxima. The shorter wave lengths are scattered more, leaving the longer ones to be transmitted along the axial beam; the brownish color is therefore the complement of Tyndall blue from a coarse structure.

The relationship between resolution and numerical aperture is strictly in accordance with the theory of diffraction, so that the dimensions of the structure may be determined from the numerical aperture of the objective which barely resolves it. The measured distance between striae, 1.6μ, is the same as the calculated limit of resolution, for axial blue light, of a 0.25 N. A. objective.

These experiments on butterfly scales deal with a diffracting system of a very simple sort. When an artificial grating is used, the results are analogous as regards the diffraction spectra, but the transmission colors are practically lacking. This is due to the shallowness of the rulings, and the consequent lessened intensity of the diffracted spectra. The weak transmitted blue from the first order spectra is masked by the intensity of the axial beam.

When the butterfly scale is surrounded by liquid instead of air, a similar loss of transmitted blue occurs, due to the decrease in diffraction and increase in intensity of the axial beam. When diffraction is thus minimized, only a faint brownish yellow transmission color (the complement of Tyndall blue) is observed.

A somewhat more complicated case is afforded by the diatom *Pleurosigma angulatum*, which possesses a very fine pattern of dots in rows 120° to each other and about 0.5μ apart. Instead of two diffraction spectra at the back aperture of the objective, at 180°, it shows six, at 60° intervals. These are not included by a 0.7 N. A. objective, and the structure is unresolvable and faintly yellow by axial transmitted light(complement of Tyndall blue). With a 0.95 N. A. objective the diatoms are bluish by transmitted light, and at the back aperture of the objective the blue ends of the six spectra are visible.

Particles of uniform diameter but not arranged in an orderly pattern constitute a more common type of diffracting system. A film of particles of sublimed As_2O_3 or sulphur may be collected on a microscope slide by the ordinary methods of micro-sublimation. Areas of several square millimeters (more than sufficient to fill the field of a moderate or high power objective) having substantially uniform-sized particles, are readily obtained.

When such a preparation is illuminated by a very narrow pencil of axial light, such as may be obtained by inserting a pinhole diaphragm below the substage condenser the beam is diffracted by the particles to give concentric zones of spectral colors at the back aperture of the objective; blue is innermost and nearest the axial beam, which itself is practically colorless. The spectra and transmission colors of such a system are less pure than those of diatoms or butterfly scales, because the particles are not so perfectly uniform in size.

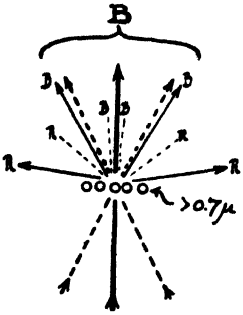

FIG. 5
Diffraction with convergent light. Blue rays overlap through a considerable angle, giving transmitted blue.

On diaphragming the objective so as to exclude successively the various colors of the diffraction spectra, beginning with the red, the transmission color, as seen in the microscopic image, varies just as in the case of the butterfly scale. As soon as the red is cut off, the particles become bluish green by transmitted light; when only the blue diffracted rays and the axial beam are allowed to pass through the aperture of the objective, transmitted blue is observed, and the structure is barely resolvable. Further diaphragming of the objective destroys the resolution. If the objective diaphragm is reduced to the point where the direct axial (undiffracted) beam fills its aperture, a distinct decrease in brightness and purity of the color results, and the transmitted blue may even be destroyed. If the structure is so fine as to cause "scattering" of blue (Tyndall blue) then the direct beam and the final transmission color will be yellow.

An illuminating beam which is somewhat less narrow, and therefore equivalent to slightly convergent or diffuse transmitted light, may be obtained by using the ordinary condenser diaphragm, closed nearly as far as possible. With such illumination the above diffraction phenomena, especially the zones of spectral colors, are much less well defined, because each "ray" of the illuminating beam follows a different path, and has its annular diffration spectrum in a different position, so as to cause them to overlap.

Within a small cone however, which is numerically somewhat less than that which just includes the blue diffracted rays with strictly axial light, only the inner blue portions of the spectra overlap. At the back aperture of the objective this is manifest as a pale blue central beam of light, which corresponds to the opening of the condenser diaphragm. If the diaphragm of the condenser is opened still further, the overlapping of diffracted spectra is still greater and the blue color of the rays within the narrow cone is masked.

With the full aperture of the objective and illumination of the degree of convergence just described, transmitted blue is not observable, because all the diffracted light is admitted by the objective to form the image. But if the objective is diaphragmed until only the blue central beam is included (that is, until its aperture is no greater than that of the condenser) the transmitted blue is strikingly evident.

The effect of particles or structures of various sizes is demonstrable by means of particles from different portions of the film of sublimate; those which have condensed at the edge of the patch of particles are finer than those nearer the material to be sublimed, which have probably grown by "digestion" after they first condensed on the slide. The finer particles, practically unresolvable except by blue light, show only a transmitted yellow, at any aperture. Where they are slightly coarser, the transmission color is orange; where still coarser, it varies through purple to blue.

When films of sublimed particles are examined by dark-field illumination, those portions which are yellow by transmitted light (finer particles) scatter blue light and appear blue against the dark ground. The areas with coarser particles (blue by transmitted light) scatter yellow. Still coarser particles (neutral gray by transmitted light) scatter white. The lack of perfect uniformity of size is more manifest in the areas of coarser particles, and the transmission color tends to be grayish and indistinct, while the color zones at the back aperture of the objective become ill-defined.

Diatoms having much more highly uniform structure (from "Celite"; unidentified) show simple perforations or markings. The transmission colors vary with the size, just as in the case of the sublimed particles, but are more distinct.

When any of the above diffracting structures are immersed in liquid, the color phenomena which depend on diffraction practically vanish, though the finer structures still show a faint yellowish transmission color (complement of Tyndall blue).

The destruction of transmitted blue when markedly convergent instead of unidirectional illumination is obtained by opening the condenser diaphragm, and the necessity for a narrow aperture objective, both confirm the character of the color as a diffraction phenomenon rather than "scattering." The relationship of the aperture of objective and condenser in order to obtain a transmitted blue when slightly convergent light is used, is also a check on this theory.

The above phenomena indicate that the appearance of transmitted blue in microscopic objects is a function of the numerical apertures of the objective and of the condenser, and that it depends on the exclusion of all diffracted spectra except first order blue. Furthermore, since transmitted blue only occurs in "contrasty" objects, it is evident that it also depends on the intensity of the diffracted spectra as compared with the axial undiffracted beam.

There appears to be no necessary reason why transmitted blue cannot be observed in relatively coarse structures, provided the aperture of the objective bears the proper relationship to that of the illumination, the dimensions are uniform, and the diffracting power is high. However, since the aperture of the objective would have to be adjusted more precisely for the "compressed" diffraction spectra from coarse structures, and since non-uniformity is more common, such cases have not as yet been observed. Probably special coarse, very deeply ruled gratings, if such were available, would serve to demonstrate the phenomenon over a wider range of sizes. The minimum dimension for transmitted blue is about 0.4μ; below this extends the range of Tyndall blue. The maximum dimension is probably about 1μ.

Transmitted Blue as seen with the Naked Eye

The explanation of transmitted blue and yellow, as produced with microscopic objects and observation, throws some light on the transmission colors of fine particles as seen with the naked eye. The sublimates of fine particles which exhibit areas of blue and of yellow by transmitted light, when viewed under the microscope, show these same areas colored to the naked eye. The colors are not noticeable, with the exception of Tyndall blue as seen against a dark background, unless the illumination is practically unidirectional. With diffuse light, as in close proximity to a white background, the transmission colors are not visible.

The yellow transmission color may be explained as simply the complement of Tyndall blue, since it occurs in the areas which show a good Tyndall blue to the naked eye. The color disappears in diffuse illumination because the particles receive light from a wide angular range, hence their transmission color, yellow, and the blue which they scatter are superposed and more or less nullify each other. Furthermore, there is not the cumulative action of superposed particles such as would be the case in a suspension of some thickness. This same reasoning applies to the disappearance of transmitted blue, and indeed to all diffraction colors.

Transmitted blue is visible to the naked eye partly because the particles may be of such a size that they actually tend to scatter yellow light fairly effectively, as shown under dark-field illumination. The complementary color, blue, is therefore transmitted. The general explanation in terms of diffraction is also applicable, for if the numerical aperture of the eye is reduced by means of a pinhole diaphragm placed close to it, the color becomes much grayer and may be destroyed just as when the objective aperture is reduced below that of the condenser. Furthermore, if the illumination is much more diffuse than would correspond to an angular aperture equal to that of the angle between the blue diffracted rays with axial light, the blue color is obscured.

Although the present paper deals only with a thin layer of particles, it is probable that the qualitative reasoning employed may be applied to relatively thick systems of particles in suspension. These are known[2] to show a similar series of transmission colors (yellow, orange, blue) when the size of the particles is approximately that which gives these colors under the microscope. There is also the cumulative effect of many layers, which, even if each particle only deviated a small intensity of light through a small angle, would tend to enhance the transmission color.

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[2] Keen and Porter: Proc. Roy. Soc., **89A**, 370 (1914); Raman: **100A**, 102 (1921); Ostwald and Auerbach: Kolloid-Z., **38**, 336 (1926).

Summary

On the basis of direct qualitative experimental evidence, rather than computations which of necessity would demand even more assumptions, the conclusions of this paper may be summarized as follows.:

1. Uniformly sized particles of structures finer than *ca* 0.4μ scatter light inversely as λ^4, and are not resolvable with axial illumination. They exhibit Tyndall blue and transmit yellow or orange, even with relatively diffuse illuminations.

2. Uniformly sized particles or structures between *ca* 0.4μ and *ca* 0.7μ scatter red light and diffract blue in maxima at such angles as to be resolvable with blue light and axial illumination. If they are of bold outlines or surrounded by a medium widely different refractive index, they exhibit transmitted blue and scatter yellow or orange, even with slightly diffuse illumination.

3. Uniformly sized particles or structures coarser than *ca.* 0.7μ diffract all wave lengths, the red more than the blue. If of good contrast, they exhibit transmitted blue, provided the numerical aperture of the objective is such as to include only the blue end of the diffracted spectra obtained with a narrow axial illuminating cone.

4. Transmitted blue, which is lost in diffuse light, is apparent to the naked eye with specimens or coarser than 0.4μ. It is due to the greater deviation of red than blue, either by scattering or by diffraction.

5. Transmitted blue, visible to the naked eye, exhibited by suspensions of fine particles, is probably explainable by the above reasoning.

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THE VAPOR-ADSORPTION CAPACITY OF SILICA GELS AS AFFECTED BY EXTENT OF DRYING BEFORE WET-HEAT TREATMENT AND BY TEMPERATURE OF ACID TREATMENT AND ACTIVATION

BY HARRY N. HOLMES AND A. L. ELDER

During the past few years a great increase in the use of porous silica gel has been noted. It has found its way into such industrial processes as the removal of sulfur compounds (and colored material) from petroleum; the recovery of gasoline from still gases, and of benzene from coke oven gases; and the drying of air, oxygen, chlorine, acetylene, ethylene, carbon dioxide, and sulfur dioxide. It is also an excellent carrier for catalysts, and is a good adsorbent in refrigeration.

Silica gel is usually prepared by mixing a dilute solution of sodium or potassium silicate with a suitable acid. Patrick[1] prepared a hard glassy silica gel by mixing hot sodium silicate of 1.185 sp. gr. with an equal volume of 10 per cent solution of hydrochloric acid. After the gel had set, it was broken into pieces and the salt and excess acid were washed out with water. The gel was then air dried. The porosity of the gel depends upon degree and rate of drying. Holmes[2] and his co-workers[3] prepared porous silica gels by first adding such salts as ferric chloride to sodium silicate solution, drying the gel thus formed to a moisture content of 55-60 per cent, and removing the iron oxide from the firm solid by treating with acid. It was noted that the porosity of the gel depended upon its moisture content before acid treatment, the acid used, and the temperature at which it was given the acid treatment. It is of interest to note that silica gels produced by Ray[4] in 1923 adsorbed only 23 percent of their weight of benzene. Wet heat-treated gels prepared by Holmes[5] have adsorbed 140 per cent of their own weight of benzene from air saturated at 30°C.

Inasmuch as the adsorption capacity of a gel is a function of temperature and extent of drying before the wet-heat treatment, the rate of drying, and the temperature and method of removing some of the constituents of the gel, it was thought that a detailed study of these factors would be worth while.

Patrick, Frazer, and Rush[6] have studied the effect of activation temperature on the adsorption capacity of pure silica gel and silica gel soaked in sodium sulfate. They found that the pure gel did not lose seriously in porosity until heated above 750°C. At 1100°C the amorphous silica gel changed to the crystalline form; due, they believe, to the atoms acquiring sufficient mobility to produce a new orientation. The gel containing sodium sulfate lost in adsorption efficiency at a lower temperature. The use of silica gel in adsorbing substances which later are removed by burning made it advisable to extend this study to include other types of silica gels.

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[1] U. S. Pat., 1,297,724.

[2] The preparation of silica gels and their use as catalyst supports are covered in U.S. Pats., 1,739,305; 1,739,306; 1,739,307; 1,665,264; and others pending.

[3] Holmes and Anderson: Ind. Eng. Chem., **17**, 28 (1925); Holmes, Sullivan, and Metcalf: **18**, 386 (1926).

[4] Chem. Met. Eng. **29**, 354 (1923).

[5] "Laboratory Manual of Colloid Chemistry," 195 (1928).

[6] J. Phys. Chem., **31**, 1510 (1927).

It has been noted that there is a tendency for the more porous gels to decrease in adsorption capacity on standing a few years. The benzene-adsorption capacities of some gels, prepared and tested years ago, were redetermined.

Apparatus

A diagram of the apparatus used in this investigation to determine the benzene-adsorption capacity of silica gel is shown in Fig. 1. Air from the compressed air tank was forced through the air-pressure regulator A, a calcium chloride drying tube B, a bottle C of concentrated sulfuric acid, a flowmeter D and through three bottles of benzene, E. E′, E″ as saturators, and a fourth bottle F containing glass wool to catch any spray. In those experiments in which the benzene-adsorption capacity of gels was measured with air saturated with benzene, the saturated air passed directly through the three-way stopcock into the adsorption tube H which contained the silica gel. In experiments in which the benzene saturated air was diluted with air containing no benzene, air was passed through a second system, A′, B′, C′, D′, (A′ B′ C′ D′ are units similar to A, B, C, D) into the first adsorption train through the stopcock G. The bottles containing the benzene and the ad-

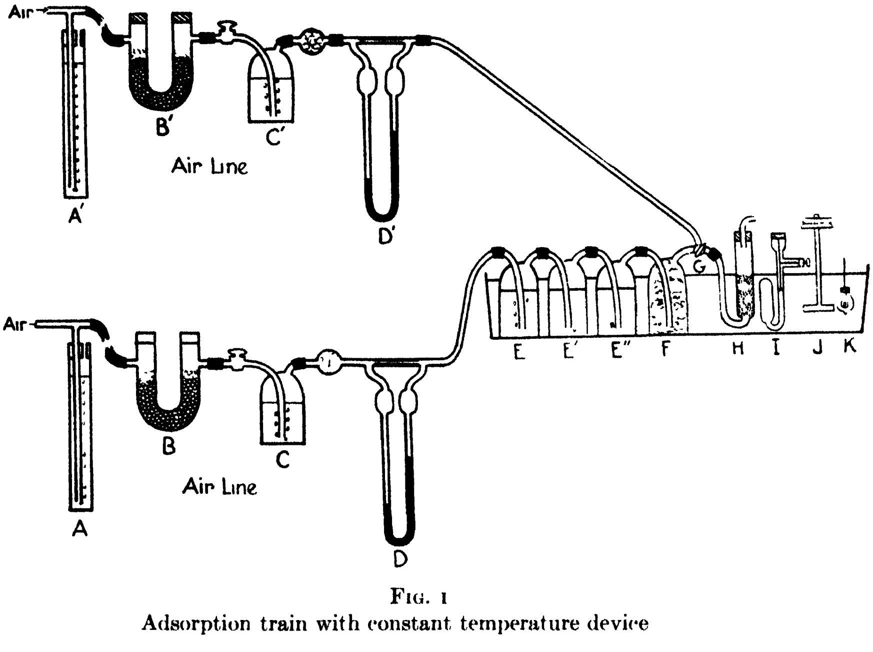

Fig. 1
Adsorption train with constant temperature device

sorption tube were placed in a water bath which was kept at 30°C by the thermoregulator I. A stirrer J was used to decrease temperature fluctuations of the water bath. K is an electric bulb used for heating the water bath to 30°C. The electrical connections are not shown in the drawing. To further decrease temperature fluctuations the water bath was enclosed in a glass case so that the air above the bath could be kept at 30°C.

In making a measurement, the sample of gel to be tested was ground to between 10 and 20 mesh, and activated by passing a stream of dried air at 140-200°C at the rate of 100 cc per minute through the gel until it reached constant weight. The activating tube consisted of a piece of pyrex tubing 2 cm in diameter and 50 cm in length, surrounded with nichrome wire the surface of which was well insulated with asbestos. The activation process required from one to two hours. After activation the gel was placed in the adsorption tube H, which was then stoppered, cooled, weighed and attached to the adsorption train. The air stream saturated with benzene was run through the tube at the rate of 100 cc per minute until the adsorption tube ceased to gain in weight. Adsorption under the given conditions by this dynamic method is calculated as per cent weight of the gel samples. Those gels which were used in the study of the effect of activation temperature on benzene-adsorption capacity were activated in a quartz tube placed in a Hoskins furnace. The activation temperature was determined by use of a thermocouple.

Effect of the Age of a Gel on Its Benzene-Adsorption Capacity

Some gels which had been bottled and kept around the laboratory for several years were used for these experiments. When the gels were first made, their benzene-adsorption capacities were determined at 30°C. These values were redetermined at a later date. The results are given in Table I for eleven different gels. These data show that as the gels age, there is a tendency for their benzene-adsorption capacity to decrease.

TABLE I

Effect of the Age of a Gel on its Benzene-Adsorption Capacity

Gel number	First Date	Per cent Benzene adsorbed	Second Date	Per cent Benzene adsorbed	Per cent Decrease
1	4/-/28	115	10/1/29	111	3.5
2	1/1/27	140	10/2/29	118	15.7
3	1/-/28	49	10/4/29	48	2.0
4	5/26/25	90	10/5/29	72	20.0
5	5/16/25	120	10/7/29	86	28.3
6	1/-/26	44	10/8/29	39	11.3
7	1/-/27	62	10/9/29	41	33.8
8	1/-/28	77	10/10/29	63	18.1
9	1/-/28	50	10/12/29	44	12.0
10	1/-/27	105	10/15/29	103	1.9
11	1/-/27	116	10/16/29	109	6.0

Sufficient information is not available to indicate the cause of the decrease in benzene-adsorption capacity. It is possible that a new orientation of the silica takes place, aided, no doubt by the water films present.

Effect of the Activation Temperature on the Benzene-Adsorption Capacity of Silica Gel

In this investigation five different gels were studied. The gels were activated at temperatures varying from 100°/1000°C for four hours and their benzene-adsorption capacities then determined. Gel 1 was known as the Holmes chalky gel. Gel 2 was prepared by treating a nickel salt with sodium silicate solution. The soluble constituents, (nickel salts, etc.) were then removed by acid treatment. Gel 3 was prepared by treating an aluminum salt with sodium silicate solution. The dried gel was then given the acid treatment. Gel 4 was prepared by mixing solutions of ferric chloride and sodium silicate. The gel was then given the wet-heat treatment to set the structure and to wash out the by-product, sodium chloride, but was not given an acid treatment. It therefore consisted of $xFe_2O_3ySiO_2.zH_2O$. Gel 5 was Patrick's commercial silica gel. The results of this investigation are given in Table II, and represented graphically in Fig. 2. These curves are similar to those reported by Patrick, Frazer and Rush[6] showing that with

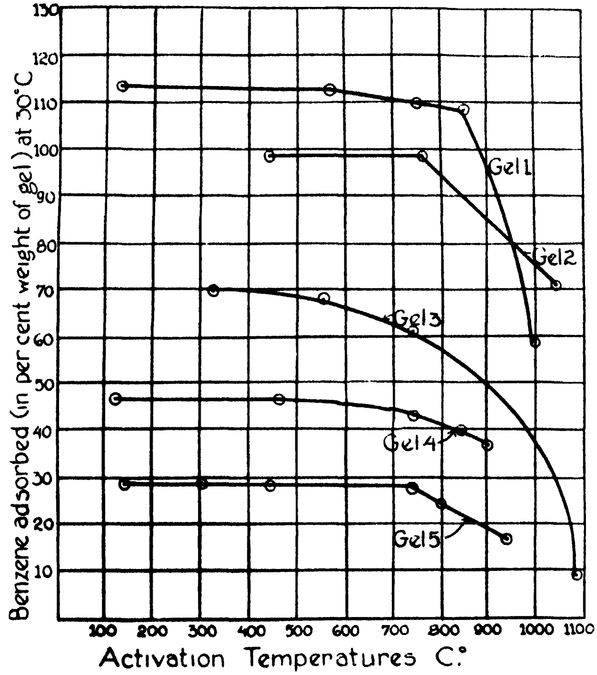

FIG. 2

Effect of activation temperature on the adsorption of benzene by silica gel from an air stream saturated at 30°C.

four of the five gels studied activation temperatures up to 800°C do not materially decrease the benzene-adsorption capacity of the gel. Any of these gels might therefore be used with safety in adsorbing material to be burned out later, or in supporting catalysts for reactions in which the temperature would not exceed 800°C. Large drops in the benzene-adsorption capacity of these gels are noted if the activation temperature is raised to 1000°C.

TABLE II

Effect of Activation Temperature on Benzene-Adsorption Capacity of Silica Gel

Gel number	Activation temperature	Adsorption in percent at 30°C	Gel number	Activation temperature	Adsorption in per cent at 30°C
1	130°	114	4	120	47
1	570	113	4	460	47
1	750	110	4	740	43
1	850	109	4	840	40
1	1000	59	4	900	37
2	440	99	5	140	29
2	760	99	5	300	29
2	1040	71	5	440	28
3	320	70	5	740	28
3	550	68	5	800	24
3	740	61	5	940	17
3	1090	9			

Effect of Variation in Extent of Drying before Wet-Heat Treatment and of Temperature of Acid Treatment on the Benzene-Adsorption Capacity of Silica Gel

The first porous gels prepared in this laboratory were made by mixing together such quantities of ferric chloride and sodium silicate solutions that the resulting filtrate was neutral to litmus. The precipitated gels were dried and given acid treatment to remove ferric oxide and then washed with water to remove the resulting soluble ferric salts and excess acid. It had been noted that if the gels were not dried to at least 60 per cent moisture content they broke into very small particles when given the acid treatment. If, however, they were dried to below 40 per cent moisture content the final gel was very hard and had lower benzene-adsorption capacity.

The "wet-heat treatment" described in a previous paper[3] depended upon the fact that gels dried to less than 70 per cent water content were so firmly set in structure by heating to approximately 100°C under water (to prevent evaporation and shrinkage) that later drying caused relatively little shrinkage. Consequently a greater porosity was secured.

To test the effect of variations in moisture content before wet-heat treatment and of temperature of acid treatment, six types of gel were made.

The first gel contained a larger proportion of ferric chloride mixed with sodium silicate than had been used previously in making the Holmes chalky gel. The second gel was prepared according to the procedure of Holmes' Laboratory Manual of Colloid Chemistry, page 193, and was practically a neutral gel. The third gel contained an excess of sodium silicate. In the other gels, copper sulfate was used in place of ferric chloride, the solution above the fourth gel being acidic, the fifth neutral, and the sixth basic.

In Table III are given the quantities of reagents used in preparing these gels.

TABLE III

Quantities of Reagents used in preparing Acid, Neutral, and Basic Silica Gels.

Gel number	2 N $FeCl_3$ in cc	N/3 $CuSO_4$ in cc	cc Sodium Silicate, Density 1 37	cc Water	Reaction to Litmus
1	15,495		3,250	75,000	Acid
2	8,000		2,500	47,500	Neutral
3	8,520		4,000	80,000	Basic
4		2,880	200	6,120	Acid
5		2,400	220	6,580	Neutral
6		2,400	320	6,480	Basic

The quantities of reagents as tabulated in Table III were mixed to make six gels which were allowed to stand 60 hours and then filtered through fine cheesecloth supported on coarse galvanized wire. The layers of fresh gel on the filter racks were about 7 cm in depth. As soon as the masses could be handled they were broken up into large lumps, dried on screens, and then broken into smaller lumps about 2 cm in diameter. Determinations of the water content of the gels were made from day to day and samples bottled at different moisture contents varying from about 40 to 60 per cent. The bottles were sealed and allowed to "sweat" or synerize for a week. Drops of solution appeared on the outside of the lumps while the gels were forming a better structure. The samples were then treated with 9N H_2SO_4 at different temperatures, washed free from the ferric sulfate formed and other soluble constituents, dried, activated, and used for benzene-adsorption experiments at 30°C. As shown in a previous paper,[3] removal of soluble iron or copper salts from a soft gel would merely mean a collapse of the gel, filling the spaces previously occupied by ferric oxide, etc. It is essential here that the gel be dried to a firm, non-collapsing condition before acid treatment, so that the space previously occupied by ferric oxide is obtained as increased porosity. The benzene-adsorption determinations are given in Table IV. The results from iron gels prepared by mixing ferric chloride with sodium silicate solution, given in Fig. 3, show that the benzene-adsorption capacity of a gel depends not only upon the ratio of ferric chloride to sodium silicate used in the preparation of the gel, but also upon the moisture content of the gel before acid

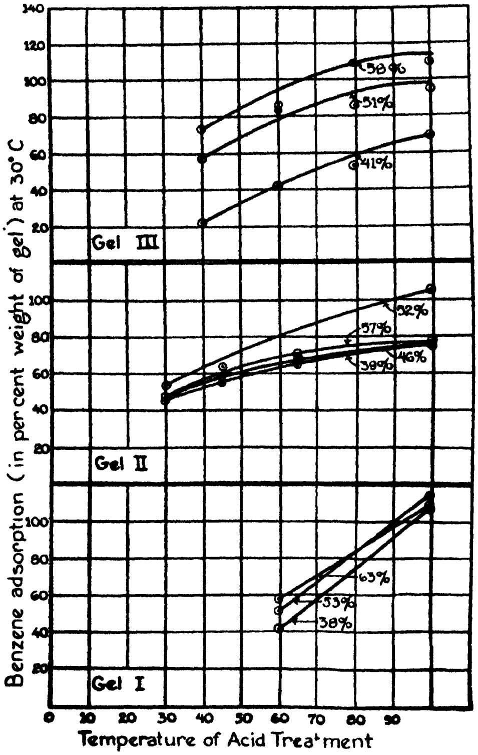

Fig. 3

The effect on adsorption of variations in the moisture-content before wet-heat treatment and temperature of acid-treatment of silica gels made from the product of mixing ferric chloride with sodium silicate. (Adsorption was from an air stream saturated with benzene at 30°.)

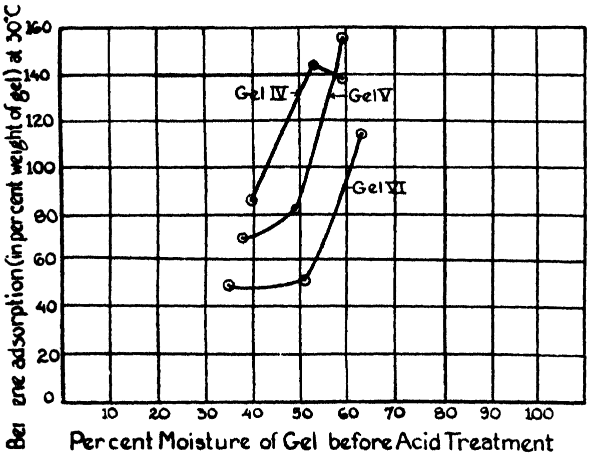

Fig. 4

The effect on adsorption of variations in the moisture content before wet-heat treatment (at 100°) of silica gels made from the product of mixing copper sulfate with sodium silicate. (Adsorption was from an air stream saturated with benzene at 30°.)

treatment and upon the temperature at which the acid treatment is applied. An increase in the temperature of acid treatment from 30°C to 100°C increases the benzene-adsorption capacity of the gel.

TABLE IV

Effect of Variation of Moisture Content before Wet-Heat Treatment and Temperature of Acid Treatment on Benzene-Adsorption Capacity of Silica Gel

Gel number	Per cent moisture content	Temperature of treatment with 9N H_2SO_4	Per cent C_6H_6 adsorbed by the gel at 30°C
1	38	60	42
1	38	100	107
1	53	60	54
1	53	100	114
1	63	60	59
1	63	100	109
2	39	30	47
2	39	45	55
2	39	65	65
2	39	100	76
2	46	30	43
2	46	45	58
2	46	65	70
2	46	100	78
2	52	30	55
2	52	45	64
2	52	65	—
2	52	100	105
2	57	30	48
2	57	45	59
2	57	65	71
2	57	100	77
3	41	40	23
3	41	60	42
3	41	80	55
3	41	100	71
3	51	40	59
3	51	60	84
3	51	80	87
3	51	100	96
3	58	40	73
3	58	60	86
3	58	80	110
3	58	100	111
4	40	100	87
4	53·5	100	144
4	59	100	140
5	38	100	71
5	49	100	82
5	59	100	156
6	35	100	50
6	51	100	52
6	63	100	115

For gels which were precipitated from acid, neutral, and alkaline solutions the highest benzene adsorptions were obtained from gels which contained 53, 52, and 58 per cent moisture respectively at the time of acid treatment.. Gel 2 was the usual type while Gel 1 was prepared with an excess of ferric chloride (acidic) and Gel 3 with an excess of sodium silicate (basic).

The data for the benzene capacity of gels made by mixing copper sulfate with sodium silicate and then removing certain constituents by acid treatment, are shown in Fig. 4. A new record for adsorption capacity of a gel was obtained with gel 5, which contained 59 per cent moisture at the time of acid treatment. This gel adsorbed 156 per cent of its own weight of benzene. The most porous gels were obtained from precipitates dried to 50/60 per cent moisture.

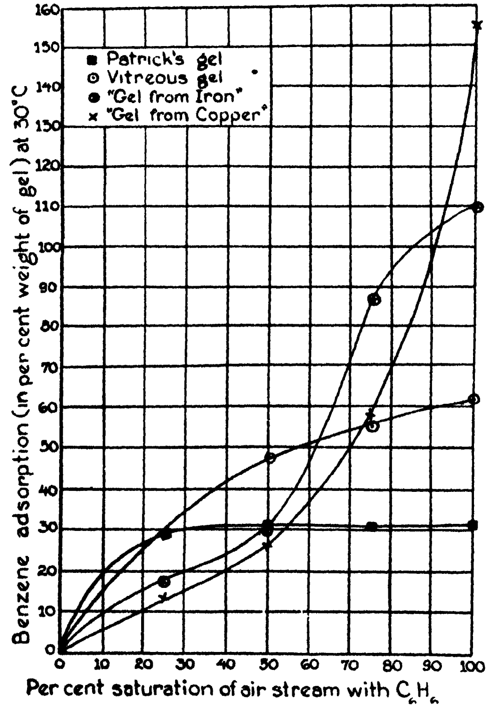

FIG. 5
Adsorption of benzene by silica gels under different partial pressures

Relation of the Porosity of Silica Gels and Their Adsorption Isotherms

Demonstration of the great increase in the adsorption capacity of silica gel due to certain variations in its preparation indicates the superior quality of the more porous gel where the volume of gel to be used must be minimized. The adsorption capacity of Patrick's gel under low partial pressures had been shown, but no comparison of the relative merits of different gels under varying partial pressures was known. To determine this factor adsorption isotherms for four typical gels were obtained. These were Patrick's glassy gel, a vitreous gel prepared by the method of Holmes and Anderson, a chalky "gel from iron" (see Table IV, gel 58 per cent water, acid treated at 100°C), and a chalky "gel from copper" (see Table IV, gel 59 per cent water, acid treated at 100°C). Adsorption curves were obtained for these four gels by measuring their capacity for adsorbing benzene from air, 25, 50, 75, and 100 per cent saturated with benzene. The data are recorded in Table V and shown graphically in Fig. 5. Patrick's gel and the hard vitreous gel were equally efficient at the lower partial pressures of benzene. The total capacity of the hard vitreous gel was double that of Patrick's. The two chalky gels are not efficient at low partial pressures. Their large internal volume indicates usefulness in economically removing most of a vapor to be adsorbed from a gas if followed in series with some hard gel with which to remove the last traces of it.

TABLE V

Adsorption of Benzene by Silica Gels under Different Partial Pressures

Gel	Per cent saturation of air with benzene at 30°C	Benzene adsorbed in per cent weight of the gel
Patrick's gel	25	29
" "	50	31
" "	75	32
" "	100	32
Hard vitreous gel	25	28
" " "	50	48
" " "	75	56
" " "	100	63
Chalky gel from iron	25	17
" " " "	50	30
" " " "	75	88
" " " "	100	111
" " " copper	25	13
" " " "	50	26
" " " "	75	59
" " " "	100	156

Summary

(1) Eleven silica gels studied showed a decrease in benzene-adsorption capacity on ageing for a few years.

(2) Four of the five silica gels examined were heated above 900°C without causing serious decreases in their benzene-adsorption capacities.

(3) Increase in the temperature of the acid treatment of a gel from 30° to 100°C increases the porosity of the gel.

(4) A gel capable of adsorbing 156 per cent of its own weight of benzene from an air stream saturated with benzene at 30°C was obtained.

(5) The most porous gels which still showed good firm structure were prepared from gels dried to 50-60 per cent moisture content before acid treatment. Useful gels may be made by first drying to a water content as low as 30 per cent.

(6) The Holmes' chalky gels have large capacities for adsorbing benzene under high partial pressures but are not efficient under low partial pressures. The Holmes' vitreous gels are practically equal to the hard glassy type at low partial pressures yet have double the total capacity of the latter at high partial pressures.

(7) Increase in efficiency of vapor adsorption by utilizing chalky gels to remove most of the vapor, followed by the use of vitreous or glassy gels to remove the last trace is suggested.

Acknowledgment

The authors wish to express their appreciation to Joseph Kanagy and Elton S. Cook for their assistance with some of the analytical work.

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THE RELATION BETWEEN PHOTOGRAPHIC REVERSAL AND THE SENSITIVITY OF THE SILVER HALIDE GRAIN

BY FRANK E. E. GERMANN AND D. K. SHEN

The use of photography as an aid to research is possibly unsurpassed by any other scientific tool. Its nearest competitor, the X-ray, would be of considerably less value if it were not possible to leave a permanent record on the photographic plate. The universal appeal of photography to both scientist and layman has brought it about that many persons have tried to explain the numerous secrets of nature associated with the making of pictures. As a result there is probably no field of science in which more amateurs are working or in which the literature is more filled with contradictory theories. However, the reason for confusion is even deeper seated than this, and may be found in large part to be due to the particular character of the science. Here if ever we deal with the chemistry of the infinitely small, and as a consequence, mere traces of chemicals which easily escape the scrutiny of the most careful analyst, may completely change the character of the results. Then again failure to realize that something added for a special purpose may have far reaching results of an altogether unexpected nature, has led to much confusion.

Our study of the grain sensitiveness of silver iodide in photographic emulsions illustrates how easily one may be led astray.[1]

The most apparent difference between silver bromide and silver iodide grains is their reducibility by means of chemical developers, a fact to which Lüppo-Cramer[2] attributes the apparent insensitivity of silver iodide.

The silver bromide emulsion, when coated in a single grain layer, usually develops very quickly with the unbromided developer, even without having received an exposure; in other words, it fogs very readily. Work carried out by previous investigators has been confined mostly to silver bromide grains, and the developers used contained a large amount of potassium bromide to suppress the development. In order to show the development centers, the development had to be stopped at the end of about a minute. We have shown that in the case of silver iodide grains in a one grain layer emulsion the development goes on very slowly; even at the end of fifteen minutes in a developer containing no soluble halide, some grains are still incompletely developed. The fact that a grain will be either completely developed or not at all was confirmed by developing the slides of an evenly exposed plate different lengths of time and counting the percentage number of grains developed, assuming a grain would be completely developed if it contained one or more centers. The plate and the exposure were so chosen that only a small fraction of the grains would be made developable, in order that fog correction, if any, could be made by having an unexposed plate developed along with it. In the short development the centers were so small that they could easily escape observation, but as the development went on, the centers increased in size until the whole grain was developed. Fig. 1 shows that the percentage number of developable grains made visible increases with time of development and becomes practically constant after about ten minutes. The values plotted have been corrected for fog, which, even after thirty minutes of development is less than one per cent. This is a very striking characteristic of silver iodide emulsions. Since prolonged developing does not increase fogging appreciably, fifteen minutes was adopted in all cases for the complete revelation of the centers. Fig. 2 shows the relation between time of exposure and percentage number of developable grains when a one grain layer silver iodide plate is exposed, developed, and examined as detailed above. It is to be noted that the maximum developability is almost reached at the exposure of 64 seconds, and that only 17 per cent of the total silver iodide grains are ever made developable. Further increase in exposure decreases the number of developable grains, that is, the period of reversal is entered.

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[1] Germann and Shen: J. Phys. Chem., **33**, 864 1583 (1929).

[2] Lüppo-Craner: Eder's Jahrb., **40**, (1903).

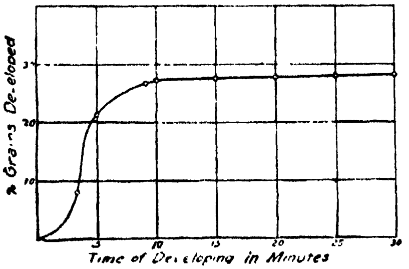

FIG. 1

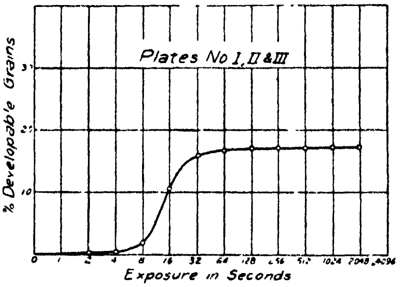

FIG 2

The relationship between sensitivity and grain size has been realized since the early days of photography. Fast emulsions usually consist of large grains, but it is not at all true that the sensitivity of any large-grained emulsion exceeds that of any small-grained one.[3] Furthermore, emulsions having identical grain characteristics may differ considerably in sensitiveness. The fact that only in one and the same emulsion,[4] are the large grains more sensitive than the small ones, makes it apparent that grain size is not the sole factor determining high sensitivity.[5] We still do not know what causes sensitivity; we know, however, that the sensitivity of an emulsion can be increased through processes which simultaneously increase the size of grains. We do not know the mechanism by which the sensitivity is increased; it seems justifiable to believe that the factors which govern the increase in

[3] Renwick: Phot. J., **61**, 333 (1921).

[4] Sheppard: Colloid Symposium Monograph, **1**, 346 (1921).

[5] Svedberg: Z. wiss. Phot., **20**, 36 (1920); Phot. J., **61**, 325 (1921); **62**, 183, 186, 210 (1922); **64**, 272 (1924); Renwick: **64**, 360 (1924); **66**, 163 (1926); Sheppard: J. Franklin Inst., **203**, 829 (1927).

sensitivity coincidently favor the growth of grains. In one and the same emulsion, the conditions under which the large grains are produced are decidedly different from those in the formation of the small-grain fraction; a difference in sensitiveness between these two classes of grains should not be surprising.

If the sensitivity is due to the presence of some impurity in the gelatin, allyl thiocarbamide, according to Sheppard,[6] and the degree of sensitivity depends upon the size of the sensitive specks situated on or in the silver halide grains,[7] the large grains would be more sensitive because the sensitive specks on the large grains are likely to be larger. If we assume that the amount of the sensitive material is limited in the gelatin, the amount adsorbed on the silver halide grain would be greater in the earlier stages of precipitation when the concentration of the sensitive material is the greatest. When an emulsion is made by pouring a silver nitrate solution into the soluble halide solution to which gelatin is added, it is obvious that at the earliest stage of precipitation, the concentration of the soluble halide is also the greatest, which favors the so-called Ostwald ripening, *i.e.*, the grains produced will attain the largest size. From these considerations, therefore, the large grains which are more sensitive are produced during the earlier stages of precipitation, during which time the concentration of both soluble halide and sensitizing material is greatest.

The insensitiveness of the silver iodide emulsion cannot be explained to be merely due to the incapability of the normal developers to reduce the silver iodide grains, as suggested by Lüppo-Cramer, because such explanation cannot satisfy the fact that seventeen per cent of the total grains are developable, unless the assumption is made that the rest of the grains are materially different and entirely lacking in sensitivity. If sensitivity is due to the presence in the grain of some foreign material derived from gelatin, then only this seventeen per cent of the total grains is supplied with such material, and the lack of sensitivity of the rest of the grains would be due to deficiency of the sensitivity material on account of the fact that they are formed during the latter stage of precipitation in which the sensitivity material is practically exhausted. If this were the case, the developable grains would have been those formed at the earlier stage of precipitation, *i.e.*, those of the largest size.

In order to test the above conclusions, two extreme fractions containing the largest and smallest grains of an emulsion were obtained by repeated centrifuging, and coated on separate glass plates. Both plates were exposed and developed in exactly the same manner; it was found that the developability-exposure curves for the large- and small-grained fractions coincided with that of the uncentrifuged emulsion. This is shown in Fig. 2, plates I, II, and III representing the uncentrifuged, large- and small-grained emulsions respectively, all of which coincide. This would indicate that the undevelopability of eighty-three per cent of the grains cannot be due to the depletion of the sensitivity promoting material in the solution. It would, furthermore, indicate that there is no appreciable difference in sensitivity between the large and small grains of the same emulsion.

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[6] Sheppard: Phot. J., **65**, 380 (1925).

[7] Sheppard: J. Franklin Inst., **200**, 51 (1925); Colloid Symposium Monograph, **3**, 86 (1925).

When one of these plates consisting of grains which were only 17 per cent developable, was bathed in a one per cent solution of either hydroquinone or pyrogallol, prior to exposure, it was found that the number of developable grains increased with time of bathing until 100 per cent was reached. Prolonged bathing in the sensitizer produced no further effect. The sensitized plate, after being thoroughly washed in running water, does not resume its initial state of low percentage developability, a fact confirming Lüppo-Cramer's early observations.[8] Metol, glycin, and amidol were also tried as sensitizers, and were found to act the same as pyrogallol and hydroquinone. Fig. 3 is a composite of many curves and shows their interrelationship better than would be possible with single ones. In cases where the same curve has various numbers, not all points are given, as there would be too much overlapping. With the scale used, practically all of the points fall on the curves, and the various curves represented by one are identical. Thus Plates I, II, and III all yield identical curves, giving a maximum developability of about 17 per cent. Plates IV and V were sensitized for ten minutes with 1 per cent hydroquinone and pyrogallol respectively, and dried without washing. The points at 4096, and 8192 seconds showing reversal, belong only to IV, the maximum time of 2048 seconds having been adopted for all other experiments. Plates VI and VII were sensitized for ten minutes in 1 per cent pyrogallol, the one being dried and then washed in running water for two hours and again dried, the other having been washed for two hours immediately after sensitizing and then dried.

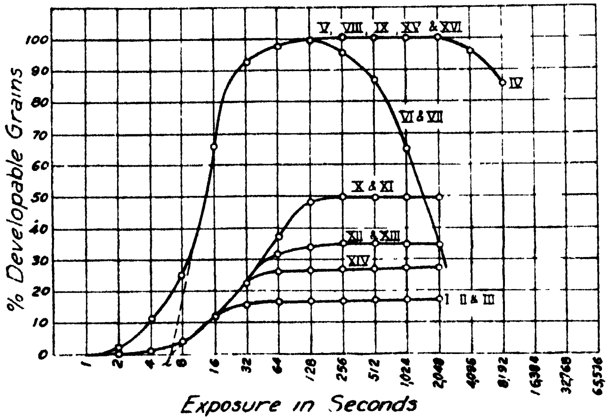

FIG. 3

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[8] Lüppo-Cramer: Phot. Korr., **38**, 158 (1901); **40**, 25 (1903).

In order to find the relative effect of sensitizers on large and small grains, Plates VIII and IX were prepared. Plate VIII consisted of the large-grain fraction prepared by centrifuging the emulsion as previously described, and Plate IX the small-grained fraction. Both were sensitized with a 1 per cent pyrogallol solution for ten minutes, and dried without washing. Thus Plate II before sensitizing corresponds to VIII after sensitizing, and similarly Plate III corresponds to Plate IX.

The power of sensitizing silver iodide plates is not limited to the usual developers, as is shown by Plates X to XV inclusive. Plates X and XI were sensitized for ten minutes with 0.2 and 0.5 per cent solutions of acetone semicarbazone respectively, and dried without washing. Plates XII and XIII were sensitized for ten minutes with 1 and 5 per cent solutions of sodium nitrite respectively, and dried without washing. Plate XIV was sensitized for ten minutes in a 1 per cent solution of sodium sulphite and dried without washing. Sodium nitrite and sodium sulphite, although much stronger halogen absorbers than the usual developers are not such good sensitizers. Plate XV was sensitized for ten minutes with a 1 per cent solution of sodium bisulphite and dried without washing. It is seen to be as effective a sensitizer as are the usual developers.

Sensitivity and Speed. The curves in Fig. 3 are similar to the characteristic curves for the various emulsions, since the percentage of developable grains is proportional to the density of the plate. When the middle, or straight line, portions of these curves, which represent the range of correct exposure, are projected until they cut the exposure axis, it is seen that they intersect at a common point marked (i). This point has been called the inertia of the emulsion by Hurter and Driffield, and may be taken as a measure of the speed. Obviously, the greater the inertia the less the speed of the emulsion. Since all these curves intersect at one point, it is obvious that the sensitizers have had no effect on the speed, but have merely increased the developability of the grains. Sensitivity is measured in terms of the amount of light that will make the grain developable. A change in sensitivity involves, therefore, a vertical displacement of the curve without changing the value of the inertia (i), while a change in speed involves a horizontal shift in (i). By sensitivity of a grain we mean that the grain is developable if a sufficient exposure is given. Speed represents the degree of sensitiveness. Obviously we cannot state that all the grains of a given emulsion have the same speed, but the average of all speeds is proportional to the reciprocal of the inertia.

The terms sensitizers and desensitizers should, therefore, be assigned to those substances which increase or decrease the developability of the grains. Substances which increase or decrease the speed should be called accelerators and retarders respectively.

The Rôle of Sensitizers. Assuming that in a given emulsion we have a wide range of speeds of the various grains, it is obvious that the grains possessing the highest speeds would be developable after a very short exposure. If the exposure is prolonged, then we enter the period of reversal for the fast grains, while at the same time making some of the slower grains developable. A wide range of speeds would accordingly yield a plate of low maximum percentage developable grains. If something can be added to such an emulsion which will prevent the reversal of those grains which have become developable, without interfering with those which have not become developable, then it should be theoretically possible to make all the grains in an emulsion developable if given a long enough exposure. This apparently is actually what happens when a sensitizer is added. When the sensitizer is not washed off, but allowed to dry in excess on the plate, the percentage number of developable grains increases to 100 per cent in some cases and remains at that value for a considerable overexposure. Finally, when the exposure is very long, the sensitizer seems to be exhausted, and the period of reversal is entered. When excess sensitizer is washed off, reversal comes quickly. *The rôle of a sensitizer thus appears to be that of preventing or delaying reversal.* If, therefore, sensitivity is merely a case of inhibited reversal, it is very possible that many substances which are at present regarded as insensitive to light may be made sensitive when suitable substances are found to prevent their rapid reversal.

The insensitivity of pure silver iodide emulsions is probably due to the existence of a wide range of speeds among the grains, combined with the phenomena of quick reversal. There might not be any inherent difference in sensitivity between grains, but we must admit that grains in a given emulsion possess different speeds. The constancy of the percentage number of developable grains in the normal unsensitized silver iodide emulsion throughout a wide range of exposures may be explained by assuming that by a given exposure those which have higher speeds may be reversed, while others are just made developable. Equilibrium may finally be reached when the number reversed per unit of exposure equals the number made developable and the horizontal portion of the curve results. If a certain critical amount of light energy is required to make a grain developable, and a definite small increment of that amount would make it reverse, the curve of the reversal should exactly repeat the curve of developability, but in a reverse direction. This is most probably the case as indicated by Curves VI and VII, Fig. 3. This simply means that the course of reversal follows exactly the rule that governs the developability of the grains.

Since the phenomenon of reversal actually takes part even in a normal exposure of a modern fast plate,[9] it becomes evident that such a phenomenon cannot be neglected in the study of photographic processes. The failure of the reciprocity law seems very likely to be due, among other factors, to the intervention of reversal.

Solarization or Reversal. Numerous theories have been offered to explain the phenomenon of reversal; the question still remains unsettled. If the action of light is to affect the grains in such a way as to initiate development, it is rather difficult to see how excessive exposure could destroy the effect already produced. The solarization cannot be the reversed reaction of that producing the latent image, because reversible reactions would come to an equilibrium as their ultimate stage. It is thermodynamically impossible that a reaction goes to completion in one direction and then completely reverses to its original state under the same external conditions. The view that the chemical composition of the solarized image is different from that of the normal latent image and that the silver halide grains having received a solarizing exposure are chemically different from the normal unexposed grains, is a very debatable assumption. Arguments of this nature will ultimately lead to the ever-present controversy over the chemical or physical nature of the latent image. In fact, we have proven experimentally that solarized grains are practically identical to the normal unexposed grains in the case of silver iodide emulsions so far as their behavior towards sensitizers is concerned. When a silver iodide one-grain layer plate which has been exposed to complete solarization is sensitized with a 1 per cent pyrogallol solution, the exposure-developability curve falls exactly on that of the similarly sensitized normal plate. This is shown by Plate XVI of Fig. 3 which was a one-layer silver iodide emulsion exposed twenty minutes to a 150-watt incandescent lamp at a distance of 0.5 meter, then sensitized with a 1 per cent pyrogallol solution for ten minutes, and dried without washing.

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[9] Svedberg: Phot. J., **64**, 272 (1924).

Photo-Retrogression. Another interesting characteristic of the silver iodide plate is its rapid photo-retrogression. On one occasion, a silver iodide plate was exposed and left undeveloped for twelve hours. On developing, the maximum percentage developable grains was reduced to half of what it would have been had the plate been developed immediately after exposure. The nature of photo-retrogression, though very little understood, is probably due to the same causes as reversal.

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THE THERMOELASTIC EFFECT IN CELLULOSE ESTER FILMS[1]

BY J. G. McNALLY AND S. E. SHEPPARD

In general, metals, as well as many other materials, are cooled, *i.e., absorb* heat, when stretched.[2] The relationship of the elastic and thermal properties of such normal materials may be summed up in the statements[3] that with increasing temperature, (a) the modulus of elasticity decreases, (b) the elasticity number or deformation increases, *i.e.*, the cross-sectional alteration increases more rapidly than the elongation; however, (c) the volume alteration decreases. This behavior indicates a relation of the elastic properties to the coefficient of thermal expansion, in fact this coefficient depends upon the stress on the material in question. From thermodynamic reasoning it follows that the temperature coefficients of thermal expansion and of elastic deformation (or of the modulus of elasticity) must have opposite signs.

Accordingly, with normal materials, *e.g.*, metals, the thermal expansion coefficient increases with increasing stress, while the modulus of stretch (Young's modulus) decreases with rising temperature.

Apparently quite contradictory is the behavior of rubber. Early observations by Gough,[4] rediscovered by Page[5] and Joule[2] showed that rubber is warmed, or develops heat, on stretching. In agreement with the previously sketched reciprocal relations of the thermal and elastic properties, and more generally, with the Braun-LeChatelier rule, Kelvin[6] predicted that stretched rubber would contract if heated; this was experimentally confirmed by Joule.

Since then a large number of investigations of the Joule effect with rubber have been made, and numerous explanations offered. A review of these researches has been made by Whitby.[7] The phenomena are complicated, and point to transitions between metal-like and rubber-like solids. The main results for rubber may be summarized as follows:

(1) Some samples of rubber show an initial cooling on stretching followed by a rise in temperature.[8] Other experimenters find only the heating effect.[9] The rate of extension has a marked effect on the thermal change: a high rate causes the disappearance of the initial cooling and an increase in the amount of heating at any extension.[10] At a given rate of elongation, a critical temperature exists above which the negative (cooling) effect is not apparent.[9]

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[1] Communication No. 445 from the Kodak Research Laboratories.

[2] Joule: Proc. Roy. Soc., London, **8**, 335 (1857); Phil. Mag., **14**, 226 (1857).

[3] Cf. Auerbach: Winkelmann's "Handbuch der Physik," I (1), 584 (1908).

[4] Mem. Proc. Manchester Lit. Phil. Soc., **1** (2), 228 (1805); Nicholson's J., **13**, 305 (1886).

[5] Silliman's J., (2), **4**, 341 (1847).

[6] Cf. Joule: Proc. Roy. Soc., **8**, 335 (1857); Phil. Mag., **14**, 226 (1857).

[7] "Plantation Rubber and the Testing of Rubber," 453 (1920).

[8] Villari: Ann. Physik, **144** 274 (1872).

[9] Schwartz and Kemp: Mem. Proc. Manchester Lit. Phil. Soc., **55** (12), 9 (1911).

[10] Chauveaux: Compt. rend., **128**, 388, 479 (1899).

(2) Rubber under low stresses expands longitudinally on heating but contracts when heated under a high stress.[11] The contraction caused by an increase in temperature is greater at a low temperature than at a high temperature and if the temperature is raised sufficiently, no contraction takes place. The temperature at which the change of sign occurs is higher the greater the load.[12] It may be mentioned that muscle fibers show many points of resemblance to rubber on thermoelastic relations,[13] but, so far as we are aware, no investigation of these has been made with synthetic organic colloids. Investigations on the birefringence of cellulose ester films under stress[14] as well as the change in X-ray diagram of these materials under stress[15] show them to have certain similarities to rubber in structure and behavior. On the other hand, it has been pointed out that their elastic behavior in some respects approaches that of metals more nearly than that of rubber.[16] We have made a study of the thermoelastic relations of cellulose nitrate and cellulose acetate films, covering both the heat changes taking place when the films are stretched, and measurement of the coefficient of thermal expansion at different temperatures and stresses.

I. Heat Changes of Cellulose Ester Films when stretched

Experimental Method

Test pieces of cellulose acetate and nitrate films were placed in a dynamometer that made a record of the stress-strain curve of the material. A multiple junction Moll thermopile was clamped to the lower jaw of the dynamometer in such a manner that the opening of the instrument was kept in contact with the flat surface of the film during the stretching. The leads from the thermocouple were attached to a Leeds and Northrup high sensitivity galvanometer, the deflections of which were read on a scale 1 meter distant while the film was stretched. By noting the time at which the stress-strain data were recorded by the dynamometer and the time at which the galvanometer was read, the thermal effect during any part of the stress-strain curve could be determined.

All test pieces were 15 cm long, 1 cm wide, and very close to 0.014 cm thick.

Experimental Results

Cellulose Nitrate: Figure 1 shows the stress-strain curve for a sample of cellulose nitrate at 18.6°C and R.H. = 55 per cent. The three curves are check runs and indicate the degree of reproducibility of the experiments. The numbers along the curves give the scale deflections in millimeters of the galvanometer at the corresponding elongation and stress. It will be seen that the *cellulose nitrate film cools on stretching up to the yield point, when it starts to warm up* and continues giving off heat until it breaks. The evolution of heat is greater than the absorption during the cooling period. This film was weakly biaxial and the test piece was cut in the direction of the residual extension, as in all of the remaining experiments on biaxial films.[17]

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[11] Van Bjerken: Ann. Physik, **43**, 817 (1891).

[12] Lundal: Ann. Physik, **66**, 741 (1898).

[13] Engelmann: "Ueber den Ursprung der Muskelkraft," 2nd Ed. (1893); McCallum: J. Biol. Chem., **14**, 96 (1913).

[14] McNally and Sheppard: J. Phys. Chem., **34**, 165 (1930).

[15] Trillat: J. phys. radium, **10**, 370 (1929).

[16] Sheppard and Carver: J. Phys. Chem., **29**, 1244 (1925).

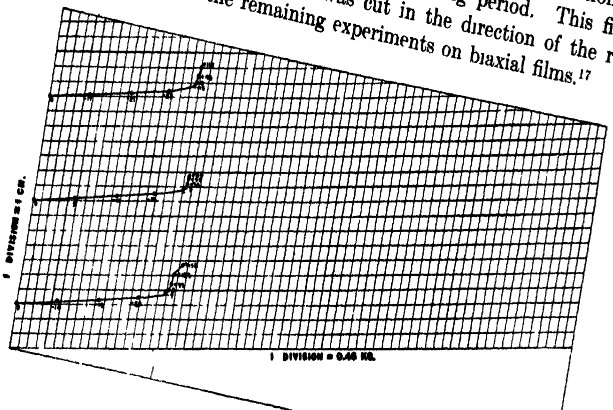

Fig. 1

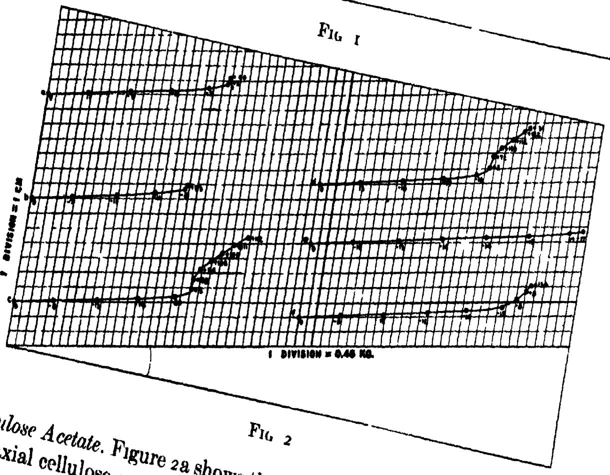

Fig. 2

Cellulose Acetate. Figure 2a shows the thermal changes observed on stretching a biaxial cellulose acetate film at 16.7° and 53 per cent R.H. The curves obtained with a uniaxial plate coated acetate film were very similar (Fig. 2b) and both are nearly identical with the nitrate film.

Elongation at Constant Rate

As mentioned above the negative heat effect changed to a positive one at the yield point. Whether this change was caused by a difference in the reaction of the internal structure of the film to stress at this point, or whether the inversion was simply connected with the rate of extension of the film, could not be determined. The following experiment was therefore carried out in which the film was stretched at the constant rate of 0.13 cm per second until the film broke. The data from this experiment are presented in Table I. θ is the scale deflection of the galvanometer. The change in sign of the thermal effect came at an elongation of about 7 per cent, which checks very closely with the extension at the yield point for this film (see Fig. 2c).

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[17] For a method of determining micellar orientation in films see McNally and Sheppard. J. Phys. Chem., **34**, 165 (1930).

We conclude, then, that the increased rate of extension after the yield point does not cause the inversion of the thermal effect.

The thermoelastic relations of another mechanically coated film are given in Fig. 2c. The curve is similar to the former. The measurements were made at 18.6° and 55 per cent R.H.

Change in Temperature

Figure 2d is a duplicate of 2c carried out at 22.4°C. This is the greatest variation in temperature it was possible to obtain under our present experimental conditions but it appears that this variation causes little if any change in the thermoelastic relation.

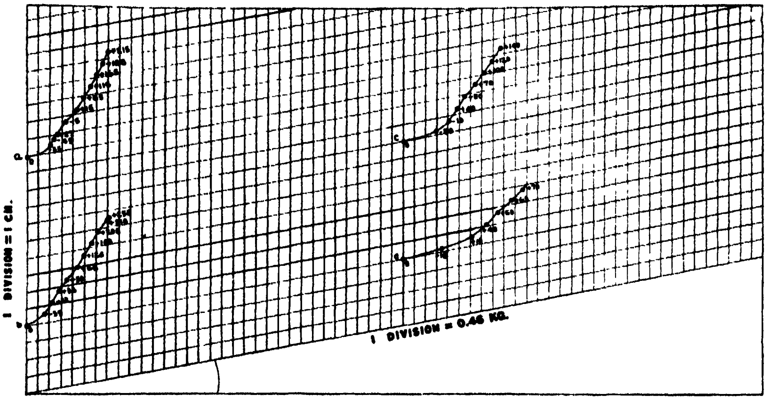
TABLE I

The Thermal Effect on Stretching Cellulose Nitrate Film at a Constant Rate of 0.13 cm/sec at 18.4°C, 50 per cent R.H.

Time sec	L cm	ΔL cm	$100\,\Delta L/L_0$	θ
0	15.00	0.0	0.0	0
1	15.13	0.13	0.86	—
2	15.26	0.26	1.72	−0.5
3	15.39	0.39	2.58	—
4	15.52	0.52	3.44	−3.8
5	15.65	0.65	4.30	—
6	15.78	0.78	5.16	−5.5
7	15.91	0.91	6.02	—
8	16.04	1.04	6.88	−1.8
9	16.17	1.17	7.74	—
10	16.30	1.30	8.60	+2.8
11	16.43	1.43	9.26	—
12	16.56	1.56	10.12	+7.8
13	16.79	1.79	10.98	—
14	16.92	1.92	11.84	+11.2
15	17.05	2.05	12.70	—
16	17.18	2.18	13.56	+13.4
17	17.31	2.31	14.42	—
18	17.44	2.44	15.28	+14.0

Coagulated Cellulose Nitrate Films Dried under Varying Tension

Figure 2e indicates the heat effect of stretching a film prepared by setting a collodion solution in water as in preparing membranes and stretching the coagulated film 10 per cent during curing. The period of plastic flow is absent and the heat evolution that accompanies it is also missing. The data from a film prepared in the same way but allowed to shrink 10 per cent on curing are given in Fig. 2f, and it is essentially the same as the air dried film. Both films were biaxial, the former very strongly so and the latter very weakly.



Coagulated Cellulose Nitrate Films with High Volatile Content

In Fig. 3 the stress-strain curves are given for a number of coagulated films. A was stretched while still containing about 50 per cent of volatile material, b about 30 per cent; c about 15 per cent, and d about 10 per cent. While the shapes of these stress-strain curves are very different, the thermal effect is still the same—cooling at low elongations and heating at higher elongations.

Conclusions as to Thermoelastic Effect

(1) It appears that at ordinary temperatures both cellulose nitrate and cellulose acetate films cool when stretched to small elongations. At higher strains (deformations) an inversion in the thermal effect takes place, and heat is evolved. This result holds both for films formed by air drying (solvent evaporation) and by coagulation (solvent extraction).

(2) If the film is stretched on drying sufficiently to become strongly biaxial, this secondary heating effect disappears.

(3) The thermoelastic properties of coagulated films are independent of their content of volatile solvent.

(4) The thermoelastic effect is the same at constant rate of elongation as under the loading conditions with a dynamometer.

From these results it would appear that cellulose nitrate and acetate films should show lower resistance to a small strain (elongation) but increased resistance to a large one as the temperature is raised. But if the material is analogous to rubber, the rate of heating and the rate of loading would determine whether or not the films would show increased or decreased resistance to stretch at higher temperatures.

II. The Thermal Expansion of Cellulose Nitrate

To fill out our knowledge of the thermoelastic properties of cellulose esters, a study was made of the thermal expansion of cellulose nitrate.

It is well known that several crystals—silver iodide and calcspar for example—have negative coefficients of thermal expansion along certain crystallographic axes. The phenomenon has also been met with in the case of strained elastic colloids, notably rubber where it has been the subject of a large number of extensive investigations. No data existed on the thermal coefficient of expansion of any of the cellulose esters so the experiments to be described were undertaken to supply this need.

Apparatus

The thermal coefficient of expansion of crystals and metals is a well-defined property of the material that depends on the mean distance between the vibrational centers of the component atoms. In the case of organophilic colloidal materials, however, the measurement of expansion coefficients is complicated by the property which the material possesses of flowing at very low stresses. Further, the rate of flow is increased by a rise of temperature so that the elongation observed on raising the temperature of a test piece is partly caused by thermal expansion and partly by plastic flow.

In constructing an apparatus to measure the thermal expansion coefficient of organic films the rate of heating of the film should be rapid and it should be possible to measure the temperature of the film accurately at any time during the experiment. Further, dimensional changes of the test piece caused by adsorption and desorption of water or solvent vapors by the film should be eliminated. Since it would be extremely difficult to keep the test piece continuously in an atmosphere of constant humidity while the temperature was changing rapidly, it was necessary to carry out all experiments at 0 per cent relative humidity, *i.e.*, with all solvent and water vapor removed from the film.

A diagram of the apparatus used is shown in Fig. 4, and Fig. 4a gives an enlarged view of the arrangement of the interior. The test piece, F, is clamped between the two clamps C_1C_2, the bottom clamp being fixed and the top one being free to slide up and down the guide rails R_1R_2 which are rigidly secured to the heavy base plate B, of the apparatus. Tension is applied to the film by the weights, W, acting over the frictionless pulley P and through the metal rod A. The elongations were measured by means of the traveling microscope M which was fitted with an ×7.5 ocular and a 4 mm objective. The microscope was focused on the micrometer slide S the lines of which were ruled 100 to the millimeter, and was illuminated by a microscope lamp not shown in the diagram. For small rapid changes in the length of the test piece it was found convenient to observe the movement of the scale, leaving the microscope in a fixed position.

The temperature of the test piece was controlled by the use of the cylindrical cooling jacket J and the nichrome wire heating coil N the cork layer I serving as an insulator. The test piece was brought to the lower limit of the temperature interval to be investigated by circulating a cooling liquid through J. Wherever possible, this was done by circulating water from a constant temperature bath by means of a centrifugal pump, the liquid entering through O_1 and being forced out through O_2. During the experiments that were carried out at low temperatures, the circulating liquid was ethyl alcohol and cooling was effected by passing the liquid through a copper coil immersed in a carbon dioxide-ether eutectic mixture. The temperature of the test piece was raised by passing an electric current through the nichrome coil N which was wound around the glass tubes G_1G_2. These tubes were attached to the inside of the guide rails at either end. The rate of heating could be controlled by a potentiometer in the heating circuit. In all the experiments described in this paper the potentiometer was so set that the temperature of the film was raised from 15 to 45° in 45 seconds. The cooling took somewhat longer, as it required about three minutes for the film to return to its original temperature; but during most of this time the film was only a few degrees above 15°, so the rate of flow was low. The temperature of the film being studied was measured by the five-element copper-constantan thermel T the junctions of which were placed inside the heating coil and were about 0.1 mm away from the film. The thermocouple leads were carried through the glass tubes G_1G_2 and out of the cylinder through a hole in the base. The ends of the thermel were connected to a Leeds and Northrup potentiometer temperature indicat-

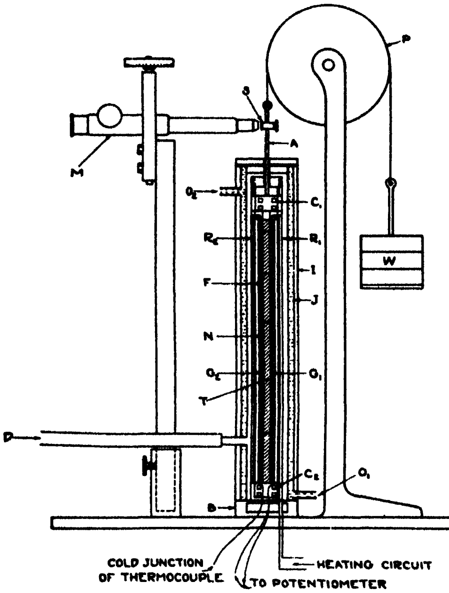


Fig. 4a

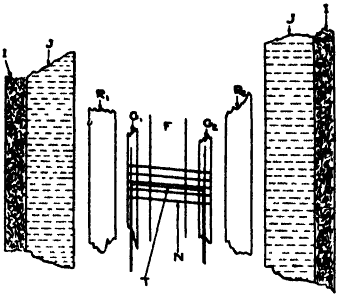


Fig. 4b

ing instrument, and alternate junctions were kept in a tube immersed in an ice-water bath. This temperature measuring system was calibrated against a Bureau of Standards pentane thermometer.

The test piece was thoroughly evacuated at room temperature before being placed in the apparatus. It was then kept in an atmosphere of 0 per cent R.H. for fifteen hours before expansion measurements were attempted. Air was passed through two sulfuric acid scrubbing towers and into the apparatus at D. A constant head of dry air was thus maintained inside the apparatus which prevented the condensation of moisture at low temperatures.

Finally, the whole apparatus was mounted on a spring suspension hung from the roof rafters of the building to eliminate errors caused by vibration. Measurements were read on scales to 0.01 mm and estimated to 0.001 mm so that a change in length of 0.0005 per cent on a 20 cm test piece could be recorded.

Materials

All of the experiments described here were carried out on a single sample of cellulose nitrate film. The film was slightly biaxial[14] and the double refraction measurements made on the film are given in Table II.

TABLE II

Double Refraction of Cellulose Nitrate Test Sample

$d = 0.15$ mm

	C Axis			B Axis	
θ	δ	δ/d	θ	δ	δ/d
0	+5	+13	0	+5	+33
10	+2	+13	10	+5	+33
20	0	0	20	+7	+46
30	−5	−33	30	+13	+87
40	−12	−80	40	+20	+133
50	−24	−160	50	+30	+200
60	−32	−210	60	+40	+266

Test pieces were cut from this film in the direction of coating so that tension was applied along the direction of stretch. The test pieces were cut exactly 0.50 cm wide by means of a slitting tool made with the two knife edges 0.50 cm apart. As mentioned above, the film was 0.15 mm thick and the original length of the unstrained test pieces between the grips was 21.20 cm.

Experimental Results

(1) *The Thermal Expansion of Cellulose Nitrate Film from 15 to 35°.*

A test piece of cellulose nitrate film was prepared and placed in the apparatus as described above. After the film had been in an atmosphere of dry air for fifteen hours, a tension of 200 grams (stress = 0.26 Kg/mm^2) was applied and the test piece was alternately heated to 40° and cooled until the retraction curve showed no hysteresis lag. This reversible effect is shown at the lowest part of the curve in Figs. 5-7. The film was then judged to be dry and free from volatile solvents. The load was increased to 1000 grams (stress = 1.33 Kg/mm^2), when the elongation measured increased by 0.22 per cent of the original length. As indicated by Figs. 5-7, heating and cooling curves show that at this stress, the film support is not perfectly elastic. The cooling curve maintains a very appreciable lag under the heating curve. As the extension and retraction cycle is repeated the difference between the elongation and retraction curves decreases until after the fifth cycle the two curves practically coincide. If, now, the load be increased to 1600 grams (2.13 Kg/mm^2) the initial hysteresis lag becomes more marked than was the case at lower stress and the form of the initial extension curve becomes concave with respect to the temperature ordinate. The curves again coincide after the cycle of extension and retraction has been repeated several times.

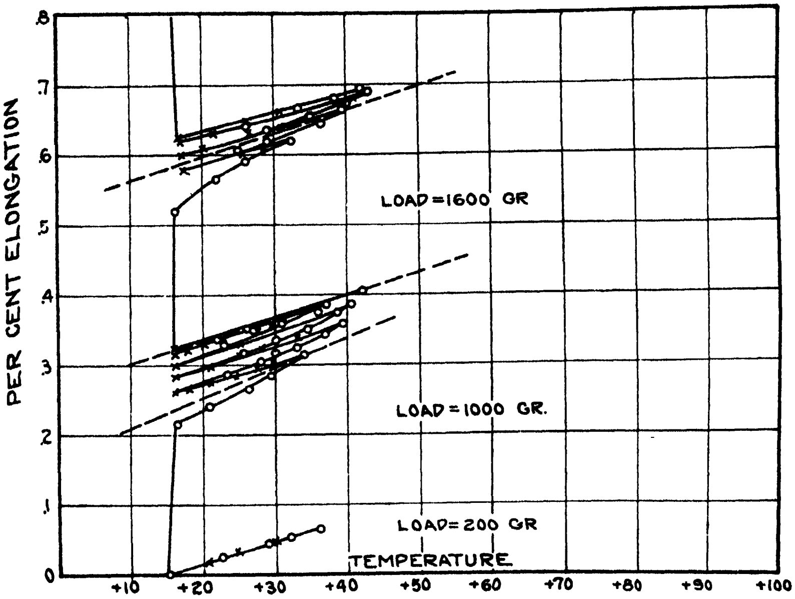


FIG. 5

As the tension on the film support is increased, a progressive series of changes takes place in the thermal expansion curves. Referring again to Figs. 5-7, it will be seen that the initial heating curve remains concave with respect to the temperature axis but the successive heating curves become strongly convex in the region where the stress varies from 3.19 to 5.05 Kg/mm^2. At the same time the retraction curves become markedly convex so that over a large portion of this region of stress, the two sets of curves intersect each other. Above a stress of 2.1 Kg/mm^2, the divergence between the final lengths reached after extension and retraction does not become appreciably less on repeating the cycle. Finally, at a stress of 7.98 Kg/mm^2, the rate of plastic flow of the material was so great that it became impossible to measure temperature effects with any accuracy with the present type of apparatus.

The coefficient of thermal expansion of the support is a poorly defined quantity as it depends on the stress acting on the film and the rate at which the heating and cooling operations are carried out. Under the conditions of our experiments the latter factor may be neglected because the error in a single determination attributable to plastic flow is negligible. While the curves are not linear, the coefficient depends on temperature interval over which it is measured and it always depends on whether the extension or retraction of the film is used for the computation. An average value for the thermal coefficient of expansion for film support may be defined by the equation:

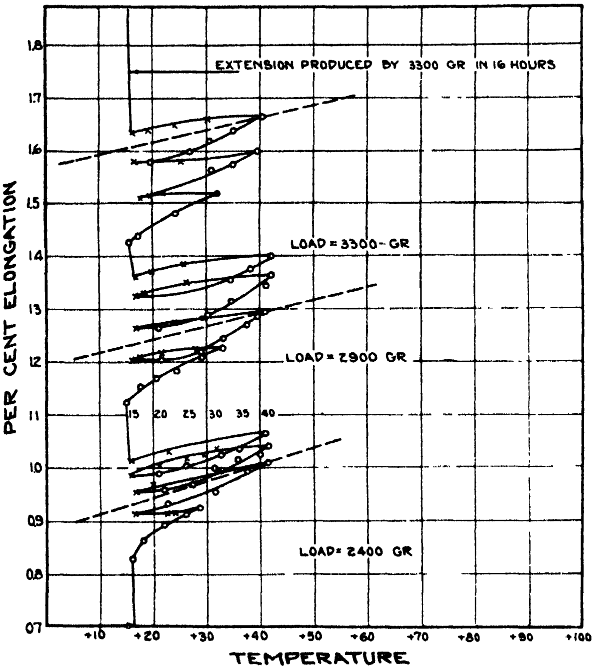


FIG. 6

$$\alpha = \frac{L_1 - \frac{1}{2}(L_0 + L_2)}{(L_0)(T_1 - T_0)}$$

where α is coefficient of linear expansion, L_0 is the length of the test piece before expansion at temperature T_0; L_1 is the length to which the film expanded at the higher temperature, T_1, and L_2 is the length to which the test strip contracted at temperature T_0. The slopes from which the values of α were calculated are shown by dotted lines in Figs. 5 and 6. Table III shows the results of such calculations at different stresses.

TABLE III

The Linear Coefficient of Thermal Expansion for Cellulose Nitrate Film between 15 and 35°

Stress—Kg/mm²	$\alpha \times 10^{-5}$
1.33	4.38
2.13	3.43
3.19	3.00
3.86	2.43
4.49	2.29
5.05	2.14

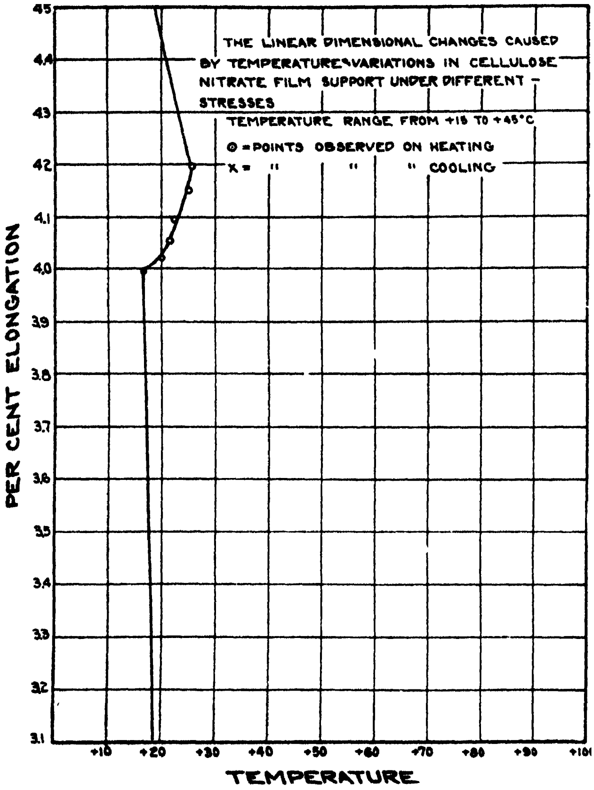


FIG. 7

The coefficient decreases progressively as the stress increases but the rate of decrease as shown by Fig. 8 decreases as the stress increases.

The influence of the previous treatment of the film on its coefficient of thermal expansion is shown in Figs. 5 and 6 by the decrease in the coefficient caused by successive elongations and retractions carried out at a constant stress. For example, at a stress of 1.33 Kg/mm², α equals 4.38×10^{-5} on the first extension-contraction cycle and 4.27×10^{-5} on the fifth. The stresses on the test pieces of the size used throughout these experiments are given on the next page, together with the corresponding load.

TABLE IV

Load—Kg.	Stress Kg/mm²	Load—Kg.	Stress Kg/mm²
0.2	0.266	2.9	3.85
0.4	0.52	3.0	3.99
1.0	1.33	3.3	4.39
1.6	2.33	3.8	5.05
2.0	2.86	6.0	7.98
2.4	3.19		

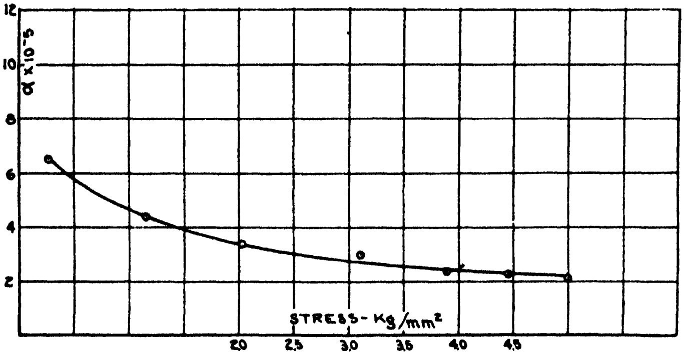


FIG. 8

The coefficient of thermal expansion of cellulose nitrate film support at different stresses Temperature interval from +15 to +45°C.

(2) *The Thermal Expansion of Cellulose Nitrate from −10 to −35°.*

The above thermoelastic studies led to the conclusion that under the proper conditions, cellulose ester films should contract when heated. The flat portions of the extension curves in Figs. 5 and 6 are probably the resultant of two opposing tendencies of the film to change its length. The first is a plastic flow tending to increase the length of the sample and the second is an elastic contraction. When the two are equal, the net resultant observed is zero.

If the above explanation of the flat portions of the curves were correct, it should be true that at low temperatures, where the rate of plastic flow was decreased, a resultant contraction of film support could be observable when the temperature of the test sample is raised. Figures 9 and 10 show the thermal extension-contraction curves of cellulose nitrate under varying stresses over the temperature range from −10 to −35°. At low tensions while the film has undergone but little strain and is sensibly isotropic with respect to the lengthwise direction, the thermal extension is positive but it has a lower value than at higher temperatures. At a stress of 0.53 Kg/mm² between −27 and −12°, $\alpha = 2.5 \times 10^{-5}$. As the film becomes anisotropic from stretching at higher stresses, the initial effect of a rapid rise in temperature of the film is to cause a contraction of the film. The negative expansion coefficient is of the same order of magnitude as the positive one, being equal to -3.4×10^{-5} at a stress of 1.33 Kg/mm^2. The initial contraction of the film support continues up to a stress of 5.0 Kg/mm^2. At higher stresses, plastic flow becomes rapid so that the effect can no longer be observed.

In the case of crystals belonging to an irregular system, α usually has very different values in different directions, calcite for example having $\alpha = +25 \times 10^{-6}$ parallel to the optic axis and -5×10^{-6} perpendicular to the axis. It seems not improbable, then, that the coefficient along and across an anisotropic film may be quite different. The values of α across certain biaxial films may be many times the values given here.

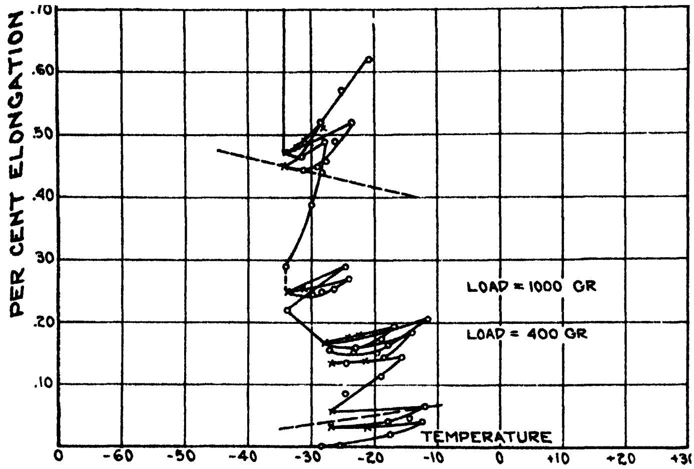


Fig. 9

The linear dimensional changes caused by temperature variations in cellulose nitrate film support under different stresses. Temperature range from −15° to −35°C.

⊙ = points observed on heating
X = points observed on cooling

Summary and Conclusions

Cellulose acetate and nitrate films that have not been subjected to large stresses on drying, cool when extended to small elongations but become warm if the extension is prolonged beyond the yield point of the material. If the structure of the film is altered by drying the film under large stresses, the region of strain corresponding to the exothermic reaction disappears. Coagulated films containing large amounts of solvent showed the same thermal behavior on stretching as the dry film, although the stress-strain relations were totally different.

The thermal coefficient of expansion of cellulose nitrate is a poorly defined quantity which depends on the stress on the material, the previous mechanical and thermal history of the sample and the temperature range over which the thermal expanison is measured. At low temperatures and at moderate stresses a negative thermal expansion was observed which is analagous to the Joule effect in rubber.

From this evidence it may be reasoned that the predominating structural alteration taking place in the film while being stretched is different in the different regions of the stress-strain curve. Possibly the cooling effect is associated with an increase in the potential energy of the micellar structure caused by an increase in the mean distance between attraction centers of the component units, this effect predominating at low strains. The exothermic change may then be evidence of mechanical dissipation of energy by internal friction in the film or a further structural change which results in a space lattice arrangement of the cellulose ester molecules and produces a thermal effect akin to a heat of crystallization as has been discussed recently in the case of rubber.[18] At any rate, the existence of the anomalous Joule effect in a dry, solvent-free cellulose ester film proves that the effect is not *a priori* evidence of a two-phase structure of the colloid, as has been suggested in the case of rubber.[19] It is also inconsistent with Wo. Ostwald's[20] explanation of

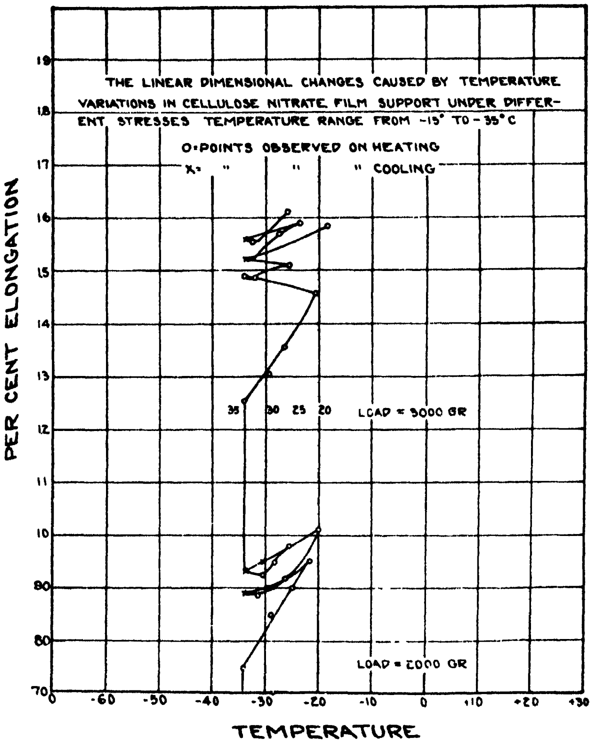


FIG. 10

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[18] Hock: Kolloid-Z., **37**, 19 (1925); Katz: **36**, 300 (1925).

[19] Freundlich and Hauser: Kolloid-Z., **36**, 15 (1925).

[20] Kolloid-Z., **40**, 58 (1926).

the structural change in rubber on stretching. Ostwald attributes the appearance of a "fiber diagram" to the deformation of a preexisting mesh or network structure in the sheaths of the latex particles. But, the parallel behavior of gelatin and cellulose esters on stretching, in approaching to or developing "fiber diagrams", makes this hypothesis unnecessary and inadequate, since the gelatin and cellulose ester films may be prepared from solutions containing only amicroscopic particles. And that is also the case with rubber from Feuchter's D-rubber (or diffused rubber sol).

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A METHOD FOR MEASURING AVERAGE PARTICLE SIZE OF EMULSIONS

BY WHEELER P. DAVEY

Experiment shows that if a drop of an oil-in-water emulsion is allowed to fall into clean water with such force as to break through the water surface the original drop of emulsion will retain its identity for some time, diffusing only slowly into the body of the water. If, however, it is deposited gently on the surface of the water without making a splash, it will spread on the water like an oil.[1] The spreading takes place with extreme rapidity and may be considered to be a two-dimensional explosion. If we assume that the layer on the surface is one particle thick and that the droplets of the disperse phase are small enough in diameter to hold a spherical shape, then the average diameter of the droplets may be measured by the apparatus which Langmuir [2] used for measuring the length of oil molecules. Trial shows that, if all other conditions of the experiment are kept constant, successive measurements of the same emulsion at different concentrations which are still of the same order of magnitude are consistent with each other and are independent of the quantity of emulsion used.

The technique of the measurement is obviously as follows. An enamelled iron tray about eight inches wide, thirty inches long and about one-fourth inch deep is filled with water. A piece of paraffined aluminum foil is floated on the surface at one end of the tray and attached to a balance such as was used by Langmuir, or to a torsion wire such as is used in the Du Nouy apparatus. The spaces between the walls of the tray and the ends of the aluminum float are sealed by constant pressure air jets. The rest of the water surface is then swept free of monomolecular layers of grease, oil, etc. by means of glass sweepers, and a drop of the emulsion is spread on this clean surface from a micrometer pipette. The area of the film is determined exactly as in Langmuir's experiments with oil films.

The calculation of particle size requires a knowledge of the total volume of the droplets of the disperse phase *as they exist in the emulsion.* Although in many cases this volume is practically the same as that of the same mass of undispersed material, it cannot be assumed that this must always be the case. The volume may be obtained by curdling a known volume of emulsion with a known volume of a solution of a suitable electrolyte, removing any included water from the curd and adding it to the rest of the water phase. The total volume of the water phase is then measured and the volume of the disperse phase is found by difference. This gives at once the concentration C of the emulsion. If V is the volume of the drop of emulsion which was spread on the water, then CV is the volume of the disperse phase in that drop. The mean diameter of the particles of disperse phase is therefore

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[1] Davey: Science, **64**, 252 (1926).

[2] Langmuir: Proc. Nat. Acad. Sci., **3**, 251 (1917).

$$d = \frac{C\,V}{A}$$

where A is the area which was covered.

The method is subject to the following limitations:

(1) The emulsion must not be so concentrated that it cannot be diluted by the simple addition of water at room temperature without vigorous stirring.

(2) The emulsion must not be so dilute that it cannot always present to the water on which it is spread a substantially continuous surface of disperse phase.

(3) The water on which the emulsion is spread must be neutral[3] (pH = 7). This condition should ordinarily be met even if it be necessary to add a buffer to the water and later make the necessary corrections as outlined below.

(4) The restoring force on the aluminum float must be very small if uncertainties in the calculated particle size are to be avoided. These four restrictions will be discussed in order.

(1) This restriction makes it impossible to use the method for determining the size of aggregates of disperse phase in concentrated emulsions which are almost ready to gel. It is obvious that the method requires the emulsion to be dilute enough so that each droplet of disperse phase can float on the water surface without being tied up with any other droplet. The method is, therefore, best adapted to measuing the size of the ultimate droplets of disperse phase. This limitation on concentration is not only due to the properties of the emulsion itself, but is due also to the practical consideration that only a small volume of disperse phase can be spread on a water surface of convenient size. The accurate measurement of the volume of disperse phase requires, of course, considerable dilution.

(2) The probable mechanism of the water-spreading of emulsions is of considerable interest. We are at first sight tempted to consider a hanging drop of an emulsion as being surrounded by a sort of bag of oriented molecules of free emulsifying agent. Such a picture may be true in some cases, but in the cases with which the writer has worked, it is hard to see why, on the basis of such a picture, the drop retains its identity when it hits the water with such force that it goes below the surface. It seems simpler to assume that at least a large part of the surface of the drop is covered with a monoparticle layer of disperse phase. This layer would correspond to the membrane around a living cell. Its existence on the surface of the drop would be consistent with the water-spreading phenomenon of emulsions which forms the basis of the method described in this paper. If such a picture is adopted, it follows that the concentration of the emulsion must be such that, as the drop flattens out on the water surface, there will be a constantly available supply

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[3] Weeks: Phys. Rev., 35, 668, (1930); See also Weeks theses for M.S. degree, The Pennsylvania State College.

of disperse phase to keep the surface completely coated. Otherwise, droplets of disperse phase would find their way into the body of the water in the tray and the measurements of particle size would not be substantially independent of concentration. It should be noted that we have dealt with extremes of concentration in (1) and (2). It is not intended to imply that our measurements of average particle size are independent of the tendency for particles of disperse phase to become aggregated as the concentration is increased.

(3) When particle-size measurements are made on water whose pH is kept at 7, the area covered by the emulsion is constant with time. If the pH of the water is greater than 7, the area covered by the emulsion (after subtracting the area covered by buffer in the same time) approaches its final value slowly, and the final value is larger than when it is measured at pH = 7. The effect is what might be expected if we assumed the extra alkali to saponify some free acid in the disperse phase, thus causing the average particle size of the disperse phase to become smaller. Besides, the soap molecules thus formed being smaller than the original particles of disperse phase, would tend to lower the average particle size. When the pH is less than 7, the area covered by the emulsion increases with time without reaching an equilibrium value, so that the disperse phase acts like a two-dimensional gas just above its critical temperature.

(4) The monoparticle layer of disperse phase floating on the surface of the water in the tray can hardly be expected to be as rigid as a corresponding monomolecular layer of a fatty acid. Excessive horizontal pressure on the layer may be expected to crumple the layer rather easily, thus giving a layer which, in some portions at least, would be more than one particle thick. For this reason, the force-area curves for emulsions do not show as sharp a point on inflection (Langmuir's S point) as is shown by fatty acids and soaps. This introduces some error in the final calculated size. Since (3) implies that the restoring force on the aluminum float lies in the optimum range for pH = 7, it is recommended that this pH be used even if it is necessary to add a buffer to the water in the tray and then correct for whatever buffer material may be adsorbed on the water surface.

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THE SPIERER LENS AND WHAT IT REVEALS IN CELLULOSE AND PROTOPLASM

BY WILLIAM SEIFRIZ

The Spierer Lens

Charles Spierer, Swiss physicist, has devised a lens for ultramicroscopic observation[1] which involves the principle that light scattered by colloidal matter is greatest in the direction of the illuminating ray (Fig. 1). It would naturally be of advantage to view matter against a dark field yet toward the source of illumination. It was Spierer's task to accomplish this. He did it by placing a small mirror in the lens system of an oil-immersion objective (Fig. 2). The illuminating rays come directly from below as in an ordinary microscope; consequently, that part of the scattered light which is of greatest intensity is toward the observer. The small mirror in the objective gives the dark field.

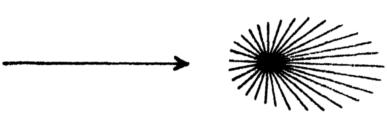

FIG. 1
The ellipse of scattered light from a colloidal particle.

The principle involves two primary prerequisites; first, the mirror must reflect all of the direct light, second; the mirror must be smaller than the lens aperture, in order to leave room for the scattered rays from the object to enter. The first prerequisite is accomplished by having the aperture of the substage diaphragm at least as small as the mirror; in practice this is 1.5 mm.

The mirror may be of gold, silver, platinum, or aluminum. In the experimental stage, and later when Spierer lenses were made by Nachet of Paris, the mirror was a piece of gold or aluminum foil placed between the lenses of the objective. The method now employed, by Zeiss, is that of electric deposition. The lens is placed behind the opening of a screen situated near the anode of a cathode tube at the opposite end of which is a cathode of platinum; the opening in the screen is of the size the mirror is to be. Platinum cathode rays are given off and deposited on the exposed surface of the lens.

Aluminum is fully opaque and gives a perfectly black field. Gold or platinum have some transparency and permit a little of the direct light to pass which is an advantage at times. The gold mirror gives a dark-green field and the platinum mirror a gray field.

The Spierer lens is an oil-immersion objective of 1.25 aperture (1/12 inch = 2.12 mm). It is provided with an adjustable iris which is useful in that it allows the observer to keep off part of the diffracted light when the diffraction phenomena are too intense and give a blurred image. (This intensity depends upon the nature of the object and of the embedding medium.) It is necessary to close this iris partially when using the latteral illumination of a cardioid condenser, otherwise the field is not sufficiently dark.

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[1] Arch. sci. phys. nat., **8**, 121 (1926).

It is sometimes of advantage to use a cardioid (dark-field) condenser in conjunction with the Spierer lens; this is not, however, necessary since the Spierer lens is itself a "dark-field," and gives very satisfactory results with an Abbe condenser, or none at all. The advantage of a cardioid condenser, when used in addition to the Spierer lens, lies in the fact that it increases the illumination of the colloidal structure by adding its share of scattered rays, which help though they do not come from the region of maximum dispersion as do those produced by the Spierer lens.

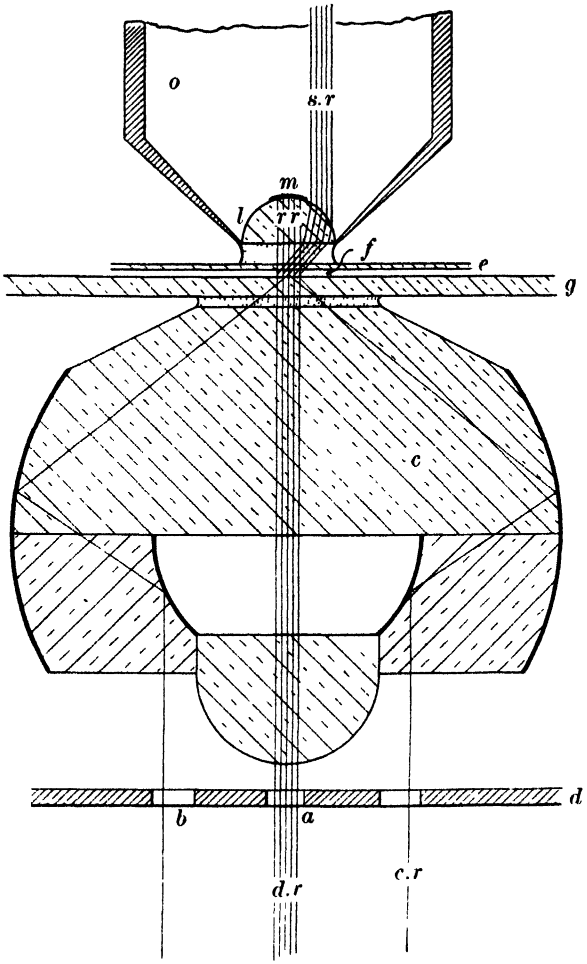

FIG. 2

The Spierer lens and special (Zeiss-Spierer) cardioid condenser: o = microscope objective; l = lower lens of the oil-immersion system; m = platinum (Spierer) mirror; $r.r.$ = reflected rays from the (Spierer) mirror, e = cover-slip, f = colloidal material; g = slide; c = cardioid condenser; d = special fixed diagraphm; a = 1.5 mm aperture for direct light, $d.r.$, to Spierer lens; b = slit for cardioid rays, $c.r.$

Spierer has combined in a special condenser the parts necessary for using the cardioid with his lens (Fig. 2). The condenser *c* contains the usual cardioid elements and in addition a fixed diaphragm *d* with a permanent aperture *a* of the desired size. This arrangement also gives perfect alignment of the illuminating ray, an important condition for the Spierer lens. The condenser possesses a movable disk which obstructs or leaves open the aperture. With the disk in the center, *i.e.*, the aperture closed, no direct rays pass through the condenser to the objective; the cardioid alone is then in use and the Spierer lens functions like any oil-immersion objective. With the disk aside, direct rays pass to both the cardioid system and the Spierer lens.

To use the Spierer lens alone, the iris diaphragm, which is part of the microscope substage and is situated below the condenser, must be closed enough to allow no light to strike the reflecting surface of the cardiod system; the small aperture in the fixed diaphragm of the condenser remains open to permit the vertical illumination to reach the Spierer lens. A simpler way, however, to use the Spierer lens alone as a dark-field lens, is to replace the special condenser by an ordinary Abbe one.

The soundness of the theory on which the Spierer lens is built is proven by the results obtained. Spierer[1] has observed a fine granular structure in dry collodion which is not revealed by any other type of optical system. The cellulose and protoplasmic structure to be told of here is also not to be seen except with the Spierer lens.

There can be no doubt that this new optical system of Charles Spierer will bring a finer structure to view than we have yet been able to see in many materials.

There are substances in which no more, in some instances less, can be seen with the Spierer lens than with the ordinary dark-field condenser. This is likely to be true where the index of refraction of the material investigated is sufficiently different from that of the surrounding medium to give pronounced optical contrast; where the surrounding medium is of nearly the same index of refraction as is the object viewed, then the Spierer lens reveals contrast and structure not visible by any other lens or system of illumination. For example, *Pleurosigma angulatum* has an index of refraction of 1.6 (that of silica); when this diatom is mounted in water (index = 1) its structure is fully visible, but when it is mounted in cedar oil, the index of refraction of which is 1.5, nothing is to be seen with ordinary illumination except the periphery. Lateral illumination (cardioid condenser) brings out considerable structure but leaves part of the diatom blank and the rest unclear; the Spierer lens reveals a much clearer structure and shows it throughout the diatom. The index of refraction of water is very close in value to that of cellulose and protoplasm; the Spierer lens should, therefore, show more of the structure of these substances than do other optical systems.

The success of work with the Spierer lens is to a great degree dependent on the nature of the medium in which the material to be studied is mounted. It is well to try air, water, glycerin, balsam, and other media before giving up, though often one is as good as another.

There is another important difference between the Spierer lens and the usual cardioid type of ultramicroscope; this is the distinction between what is light and what is dark in the two cases. If we view a bacterium with a cardioid condenser, only the edges of the minute object are bright; the interior, the bacterium itself, is dark. The same object viewed with the Spierer lens reverses things, the edges are dark and the bacterium light(since the material is transparent); in other words, the Spierer lens gives, in a sense, a "Roentgenogram" of the *interior*, while the cardioid only *illuminates* the object, giving a "photogram" of the whole.

Experimental

The observations to be reported here are restricted to the cellulose walls of the dead pith cells of *Sambucus* (elder), the dead and living epidermal leaf-cells of *Allium* (onion), the stalk of *Apium* (celery), and the protoplasm of the living cells of *Allium*. Some of the results were obtained in cooperation with Mr. Spierer in his laboratory in Geneva. I am greatly indebted to him for his technical assistance and continued interest in my work which involves the use of his lens.

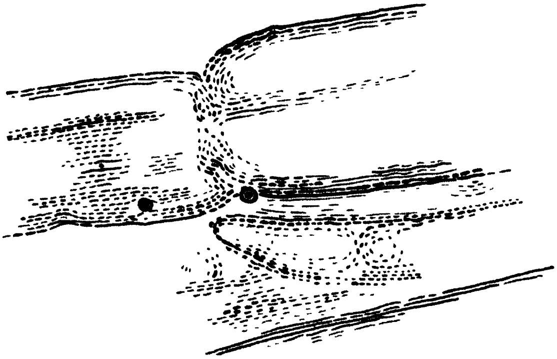

FIG. 3

Cellulose wall of dead elder pith cells showing end-to-end orientation of linear micelles in parallel striae, surface view.

Since writing the first draft of the manuscript of this article I have learned from Mr. Spierer that he too has continued our first investigations on the cellulose walls of plant cells, and obtains confirming results on such other material as the leaves of *Cichorium* and *Plantago.* With Mr. Spierer's kind permission I shall incorporate some of his findings in with our original and my recent ones.

Cellulose. The ultramicroscopic[2] structure of the cellulose walls of both dead and living plant cells is characterized by linear arrangement and discontinuity (Figs. 3 and 6). The linear arrangement is of parallel striae; the discontinuity is due to the presence of small rod-shaped particles oriented end-to-end (Figs. 3, 5, 6, and 9). The striae usually run parallel to each

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[2] In this article I shall use the word ultramicroscopic simply to mean what is seen with the Spierer lens or other dark-field system without reference to size of structural units.

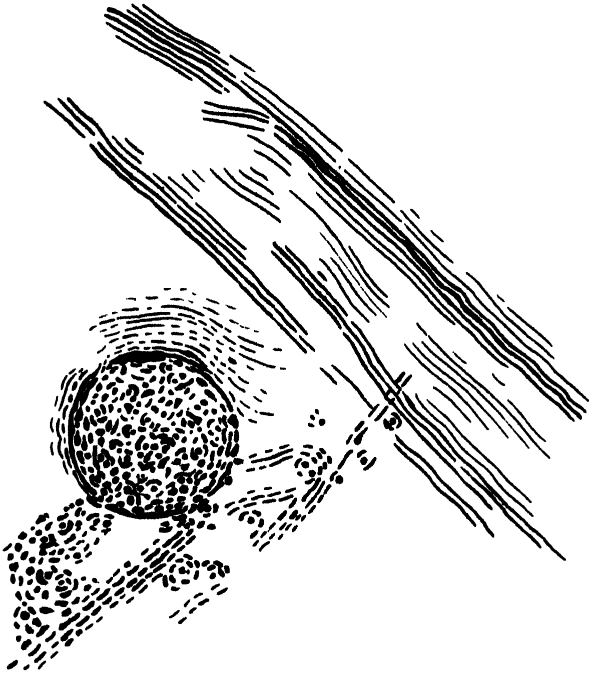


FIG. 4
Cellulose (parallel lines, upper right), protoplasm (broken lines, lower left), and nucleus (spotted circle) of living onion cell (nucleus is 20μ across).

other with only occasional irregularities. The general arrangement of the striae is often strikingly symmetrical (Figs. 7 and 8). At times, the striae run at right angles to or even cut diagonally across each other.

There is little difference to be seen in the ultramicroscopic structure of the epidermal walls of elder, onion, and celery, nor does it matter (as regards structure) whether the material is mounted in balsam (Fig. 3), in water (Fig. 4), or in air (Fig. 7). In some instances, the discontinuity of the striae, *i.e.*,

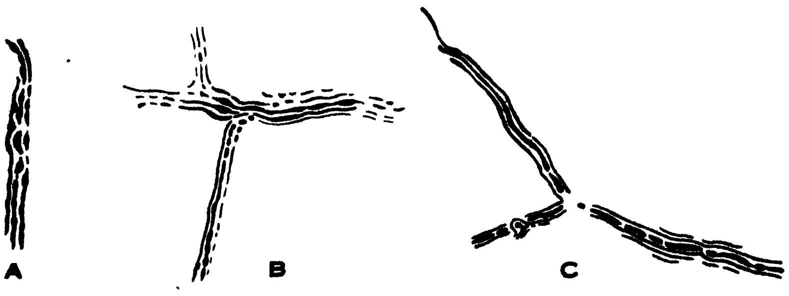
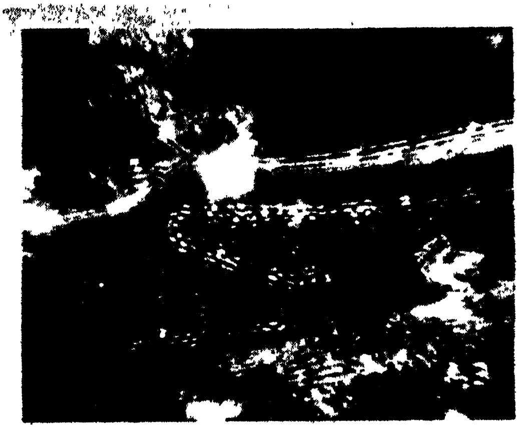
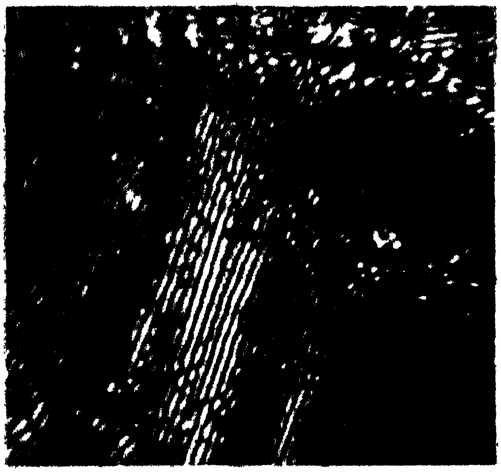


FIG. 5
Detail drawings of cellulose structure showing micelles and striae: A. from cell wall shown in Fig. 3 (elder), B. from cell wall shown in Fig. 4, C. optical transverse section of vertical walls at junction of three cells in onion epidermis (see Photo. 2 for same view with dimensions).





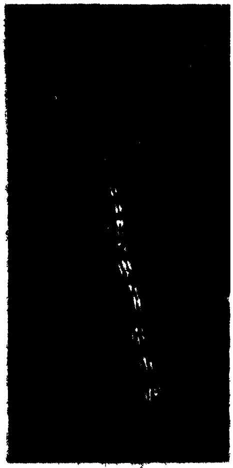


FIG. 6

Micellar structure of wall of elder pith cell seen in surface view (same view as lower half drawing, Fig. 3.)

FIG. 7

Striated structure of the dry cellulose wall of a dead onion cell, surface view.

FIG. 8

Parallel striations of cellulose wall of onion cell, surface view: note lobbed appearance of striae, the result of a micellar structure which is here less marked than in Fig. 6.

FIG. 9

Detail of transverse optical section of vertical walls at junction of three onion cells: the first rod (compound micelle) from the junction in the tail of the "Y", is 5μ, the second, 3μ, and the third 2.3μ long; the total thickness of a vertical wall, consisting of four striae, is 3μ (see Fig. 5c for drawing of this same view) the presence of short rods in the cellulose, is lacking (Figs. 7 and 8), though often the same cell may show continuous striae in one region (Fig. 4) and discontinuous ones in another region (Fig. 5, c). Furthermore, though separate rods are sometimes not present and the striae are unbroken lines, yet such striae are nearly always lobbed or undulating, as if built of distinct particles (Fig. 8).

The striae average from 0.5 to 0.7μ in thickness. The rod-shaped particles which build up the striae, vary in size, though they average rather close to 1 or 2μ in length; some, however, are two or three times this size, and some are no longer than broad (0.7μ). The longer ones are probably, like the long unbroken striae, built up of several unit particles. The 1μ rod-shaped units are not of the order of magnitude which Nägeli had in mind when he gave us the term micellae. The units of these stiae are super-micelles.

A striated appearance in the cellulose walls of plant cells is no new observation. Strasburger[3] in 1882, pictured fine striations in the walls of plant cells. These markings are visible with an oil-immersion lens and direct illumination. They have long been believed to be due to the rhythmic deposition of cellulose by protoplasm. These linear markings seen by earlier workers may be comparable to the striations described here but they, first, lack the discontinuous feature, and second, have been described for transverse optical sections of *vertical* walls and not for the *surface* view of *horizontal* walls. There are, however, parallel markings to be seen on the surface of cell walls when viewed with ordinary, direct, illumination. These are quite another thing; they are twice as coarse as are the striae seen with the Spierer lens. Spierer, in his continuation of our original joint work, has paid special attention to the distinction between the coarser microscopic striations and the finer "ultramicroscopic" ones. I shall, therefore, quote, in part, from him (which is done with his kind permission).

It is possible to pull the epidermis of plant tissue off in such a way so as to have only a single layer of cellulose, *i.e.*, the upper wall of the epidermal cells. This cellulose membrane Spierer macerated for six months in water, sometimes slightly alkaline, sometimes slightly acid, and sometimes neutral. It was thus freed entirely from cytoplasmic residues. The membrane was also, in some cases, boiled. In every instance a structure composed of long super-micelles was to be seen with the Spierer lens, but with no other system. The markings which are visible with direct illumination have nothing to do with the intimate structure of cellulose. These coarser markings result, apparently, from a very fine folding (undulation) of the membrane. As a rule, they are transversal, (*viz.*, perpendicular to the large axis of the cell), and if a pull is exerted on the membrane, these markings disappear entirely, or take the opposite direction, becoming longitudinal on account of the pull. The true micellar structure does not disappear when the membrane is stretched. When the membrane is examined carefully by changing the adjustment of the Spierer lens, the folds are recognized separately from the micellar striae.

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[3] "Zellhäute" (1882).

Question naturally arises over the actuality of these striae and rods, as, indeed, of any structure "seen" with dark-field illumination; thus, Fierz-David[4] working with a cardioid condenser, finds a "parallel" structure in artificial silk (cellulose) and natural silk. He observed a granular appearance in one of his preparations and frankly states that he regards it as not real but as an optical artifact. One cannot get an artifact without something to get it from; while of course, this does not preclude having artifacts, yet one should not be too ready to disregard them but rather be prepared to interpret them.

First, in regard to the striae, the evident criticism here is that these are diffraction lines. Observations on living protoplasm, where the striae are in motion, clearly oppose such a criticism. Furthermore, diffraction rings occur at the edges of objects; the ultramicroscopic striae of cellulose cover the surface. The following test finally eliminates diffraction phenomena as the cause of the observed striae.

The Spierer lens contains an adjustable iris; diffraction lines are eliminated when the iris is closed. In the classical test object, the diatom, *Pleurosigma*, all detailed structure disappears when the iris is closed (the *Pleurosigma* surface and contours remain visible from diffused light); the observable *Pleurosigma* structure depends, therefore, mainly on diffraction effects. The striated cellulose structure in plant cell walls, remains unaffected when the lens iris is closed, proving that this structure is not entirely dependent on diffraction but is and remains visible by diffused light.

As for the structural units of the striae, the super-micelles, continued study of them under differing conditions leaves little doubt of their reality. Cellulose would not show optical discontinuity without a structural background which possesses certain discontinuous features. Also, I find it difficult by any change in illumination to eliminate the very marked broken appearance of the parallel striations; nor does focusing up and down reveal a structure of which the rods might be the "cut" ends. Personally, I do not doubt but that the discontinuity in structure shown by the Spierer lens is a real picture of the ultramicroscopic structure of the cellulose of plant cell walls.

It was my intention to compare photomicrographs of the same material taken, first with direct illumination, then with the cardioid condenser, and then with the Spierer lens, but the picture which direct light gives with an oil-immersion lens is so pale, and the structure to be seen with the cardioid condenser so blurred when compared with the beautifully clear-cut picture given by the Spierer lens, that photographic comparison would be useless. I can, however, state with emphasis that the micellar structure pictured in the illustrations of this article are not to be seen with ordinary (direct) illumination, nor with the cardioid condenser, but only with the Spierer lens.

Protoplasm. While observing the cellulose walls of living plant cells, I often found it difficult to tell whether the lens was focused on wall or inner protoplasm. This was difficult chiefly because the protoplasm seemed to have essentially the same type of structure as the cellulose walls. How marked the resemblance may be is to be seen from Fig. 3 of cellulose and the lower half of Fig. 4 of protoplasm. The difficulty of distinguishing protoplasm from cellulose can be overcome by macerating the tissue and ridding it of protoplasm, as did Spierer, or by plasmolyzing the cells (protoplasts), that is to say, causing the protoplasm to shrink away from the cell walls by dehydrating it in a hypertonic solution. This will leave part of the cellulose walls free from protoplasm.

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[4] Naturwissenschaften, 17, 703 (1929).

Partially surrounding the nucleus (the large sphere in the center of Fig. 4) are concentric layers of cytoplasm, each built up of short rod-shaped particles. This is protoplasmic material. Where the protoplasm is stretched into strands—protoplasm often forms strands within a cell extending from wall to wall or from the nucleus to all the walls—the linear orientation of the rodlets is very pronounced (Fig. 4, below the nucleus), so much so that it is difficult, on the basis of structure alone, to distinguish a protoplasmic strand from cellulose.

The nuclear material (Fig. 4) shows no linear orientation of structural units; we have to do here with a fine emulsion.

The linear arrangement of rods in living protoplasm is, under favorable conditions, very marked. The rods are light gray in color (translucent) and the background black. The linear masses are separated from each other by distances shorter than their length, as in cellulose, and they retain their relative positions, even while the protoplasm is streaming.

The question, What fills the interstices of a group of micelles? has been considered by chemists in relation to cellulose, but, I believe, not definitely answered. The same question arises in the case of protoplasm, but here it is more easily answered, and with more certainty, though perhaps with no more satisfaction to the chemist. The black and optically structureless background, which constitutes, in a sense, the dispersion medium of the visible rod-shaped particles, is one of the constituents of the complex mixture which we call protoplasm. Indeed, of these two main components, the visible gray rods and the invisible black substratum, the latter is probably of primary importance. I believe this to be true because foreign globules (of fat) are carried by the ground substance quite independent of the visible rods. Scarth[5] supports this in stating that only a portion of protoplasm moves (by which he must mean that only a portion exhibits *active* movement). The rods, revealed by the Spierer lens, move, as do foreign globules also, but their motion is a passive one; they are carried by the active component, the black optically empty background.

As in cellulose, the discontinuous character of the protoplasmic striae is not always evident. The parallel lines are often continuous, but only in quiescent protoplasm. Whether this, as in cellulose, is a true structural feature, *i.e.*, the semi-fluid protoplasmic rods have fused, or an optical impression, cannot be definitely said.

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[5] **Protoplasma, 2,** 189 (1927).

We have, then, two main constituents of protoplasm, when viewed with the Spierer lens, the one, bright illuminated rods, oriented end-to-end in parallel lines; the other, an optically structureless material filling in the interstices of the rods. Perhaps these two materials are comparable to Strasburger's distinction between *trophoplasm*, the less active nutritive component, and *kinoplasm*, the active, irritable component.

We are still much in the dark over the ultramicroscopic structure of protoplasm, and I hesitate to compare too closely the rods seen in protoplasm with those seen in cellulose. In form and general appearance, they are almost identical, but in cellulose they are apparently the primary component (the nature of the intermicellar substance in cellulose being in doubt), while in protoplasm the rods are very likely of secondary importance. We must, however, grant that the remarkable similarity in the structure of protoplasm and of cellulose in living plant cells, as revealed by the Spierer lens, is a very striking one.

Discussion

Historical. Nägeli, in 1864, advanced the hypothesis that the structural units of cellulose cell walls are linear, anisotropic, crystalline micelles. This hypothesis, which was extended to include other colloidal systems of the lyophilic (gelatin) type, has been critized and discarded from time to time; it is probably not applicable to all lyophiles. As for cellulose, the Nägeli hypothesis is substantiated by the investigations presented here.

Full support of both the micellar and the striated structure of the cellulose walls of plant cells as revealed by the Spierer lens, is to be found in a brief survey of the literature.

As for the striae, in addition to the findings of Strasburger[3] and Fierz-David[4] already referred to, Anderson,[6] working more on the chemical side, finds that the outer wall of the epidermis of plant tissues is built up of alternate layers of cellulose and pectin.

The prevailing botanical opinion, that the lamellae of plant cell walls are the result of a rhythmic deposition of cellulose by the protoplasm, may explain the presence of certain layers composing the walls of cells. I would rather not question too critically so old a botanical hypothesis which may be true in part; however, rhythmic deposition is not the cause of the striae illustrated here. It cannot be, since the striated structure is as pronounced when seen in surface view, the plane of the supposed rhythmic deposition, as in traverse view.

As for the micelles, in spite of the severe criticism to which their existence has been subjected in recent years, subsequent work continues to bring substantial support to the micellar hypothesis of the structure of certain lyophilic systems, notably cellulose.

The cellulose "molecule" is a chain of some forty anhydrous glucose rings. Sponsler and Dore[7] were the first to indicate, by X-ray studies, a chain structure of cellulose. These chains are bundled together into fascicles, to which Meyer and Mark[8] have given the old Nägeli term "micellae," which may, in cellulose, be regarded as "crystallites" since the internal arrangement of the chains is orderly. We recall that Nägeli found cellulose anisotropic. Frey,[9] working on the submicroscopic structure of the cellulose walls of bast fibers and other plant cells, finds them to consist of distinct micelles which are strongly anisotropic, optically like rhombic crystallites, and seven times as doubly refractive as quartz.

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[6] Jahrb. wiss. Botan., 69, 501 (1928).

[7] Colloid Symposium Monograph, 4, 174 (1926).

Clark,[10] on the basis of X-ray studies, finds cellulose to be built up of oriented colloidal micelles which are bundles of long primary valence chains. On the basis of such a structure Clark gives a rational interpretation of the physical and chemical properties of cellulose fibers.

The work of Sheppard and McNally,[11] and also that of Hatschek,[12] gives support to the possibility of a micellar structure in gelatin, the substance which has been the center of the micellar controversy. Sheppard concludes that the birefringence of gelatin films is due to the orientation of symmetrical molecules or micelles, but whether the micelles are truly multimolecular or simply macromolecules cannot be stated. Seifriz[13] has carried this conception of a fibrous structure of cellulose and related systems over to living protoplasma.

Size of Micellae. Chemists regard the micelle as a bundle of chain molecules. No limiting size is given to this bundle, nor can this be readily done, any more than one can specify dimensions for a crystal (the micelle of cellulose is a crystallite). Yet, the cellulose micelle is assumed to be of ultramicroscopic dimensions. Biologists, on the other hand, have characterized as micelles particles well above the visual limit of the microscope whether or not they have viewed these particles with an ultramicroscope. It might be well to arrive at some understanding as to what the term micelle shall denote, even though we may be forced to conclude that a micelle is no more capable of precise limitation as to size than is a crystal.

The size of cellulose crystallites varies within limits generally placed at 100—200 A. U. long and 50-75 A. U. thick. An exceptional maximum length is 600 A. U. for the crystallites of ramie fiber. Even this size is much smaller than the 1μ super-micelles visible in the cellulose walls of plant cells. We must, therefore, be dealing with a larger unit in the visible (dark-field) structure of cellulose. These super-micelles are probably aggregates of crystallites. This idea is supported by Herzog[14] who states that a number of micelles may come together to build up larger structural units which he calls secondary particles.

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[8] Ber., **61**, 593 (1928); see also Mayer: Naturwissenschaften, **16**, 781 (1928).
[9] Jahrb. wiss. Botan., **65**, 195 (1926).
[10] Ind. Eng. Chem., **22**, 474 (1930).
[11] Colloid Symposium, **7**, 17 (1929).
[12] Kolloid-Z., **35**, 67 (1924); **36**, 202 (1925).
[13] Am. Naturalist, **63**, 410 (1929).
[14] Z. angew. Chem., **34**, 385 (1921).

It is at present impossible to say whether the "secondary particles" of Herzog and the super-micelles of microscopic dimensions described and pictured here, are aggregates of primary crystallites, or represent the continued growth of a crystallite; in other words, is the inner structure of a super-micelle a continuous and uniform distribution of chain molecules, or is it a larger bundle of primary crystallites? Without answering this question definitely in favor of an intermediate unit, I believe that while our knowledge of cellulose structure is still vague, we should tentatively recognize several possible sizes of micelles, if we wish to use the term in its broadest sense. The true or primary micelle is the crystallite of Meyer and Mark (200 × 50 A.U.); above this there may be a continuous series from the "secondary particle" of Herzog to the microscopic super-micelles described here (1 × 0.5μ).

Summary

1. The Spierer lens is an oil-immersion objective in which is inserted a mirror, smaller than the lens, which reflects all direct light coming into the objective. Scattered light is picked up by the lens around the mirror.
2. The structure of cellulose (and protoplasm) as revealed by the Spierer lens is that of tiny rods or super-micelles, arranged end-to-end to form long and parallel striae.

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ULTRAFILTRATION AS A TEST FOR COLLOIDAL CONSTITUENTS IN AQUEOUS AND NON-AQUEOUS SYSTEMS

BY J. W. McBAIN AND S. S. KISTLER

One of the most important tools in the study of colloids is the ultrafilter devised by Bechhold and developed by later workers.[1] Sometimes it constitutes the only direct proof that certain matter is in the colloidal state. It is not sufficiently realized, for example, that the ultramicroscope is comparatively disappointing, because most of the important stable colloids and all of the jellies may be prepared in such condition that they are invisible even in the best ultramicroscopes.[2]

The usual ultrafilters are in the coarser ranges with pores whose sizes extend from those of bacteriological filters down to moderately small colloidal particles. The ultrafilters in which the writers have been specially interested continue the series down to the dimensions of very small single molecules.[3] McBain and Jenkins[4] found it possible to utilize ultrafiltration for the measurement of osmotic pressure, hydrolysis, determination of the amounts of crystalloidal and colloidal forms, respectively, measurement of the solvation of the colloid, and even for the separation of ordinary soap micelle from ionic micelle. With a membrane such as was used for the last named purpose it should be possible to determine the hydration of each of the colloidal constituents in the solution separately. The writers have used even finer filters which hold back such molecules as sucrose or potassium chloride, while still allowing methyl alcohol and water to pass through freely.

There is a distinct limit to the denseness of membranes made from collodion, and collodion is too reactive for many purposes. It is therefore very fortunate that, as we have repeatedly emphasized, ordinary commercial cellophane provides a convenient and very finely porous ultrafilter. Cellophane is as chemically indifferent as ordinary filter paper. It is made from viscose and consists of cellulose with a trace of glycerine.[5] We have shown that its pores may be made as small as desired by filtering through it viscose cellulose dissolved in Schweitzer's reagent, or collodion dissolved in ether-alcohol. Commercial cellophane[6] is supplied in large sheets with the thickness designated by numbers ranging from 250 to 2400. Some of the thicker samples appear to be laminated and tend to separate on soaking in water. Cellophane 600 appears to be the most suitable for general use. It needs only to be swollen in water for filtering aqueous solutions, holding back all but the finest colloidal particles. It may be used with any non-aqueous solvent, but first it is necessary to displace the water by mixtures of mutually miscible solvents until finally only the desired solvent remains in the membrane.

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[1] Bechhold: Z. physik. Chem., **60**, 257 (1907); **64**, 328 (1908); Brown: Biochem J., **9**, 320, 591 (1915); **11**, 40 (1917); Elford: Brit. J. Exp. Path., **10**, 126 (1929); Proc. Roy. Soc., **106B**, 216 (1930); Krueger and Schultz: Proc. Soc. Exp. Biol. Med., **26**, 600 (1929); Krueger and Ritter: J. Gen. Physiol., **13**, 409 (1930).

[2] McBain· Colloid Symposium Monograph, **4**, 7 (1926); Kolloid-Z., **40**, 1 (1926).

[3] McBain and Kistler: J. Gen. Physiol., **12**, 187 (1928); J. Phys. Chem., **33**, 1806 (1929); Trans. Faraday Soc., **26**, 157 (1930); Brukner [Z. Ver. deut. Zucker-Ind., **76**, 3 (1926)], using Zsigmondy's commercial Ultrafein-filter impregnated with copper ferrocyanide, reported that sugar became concentrated in the molasses which they were filtering.

[4] J. Chem. Soc., **121**, 2325 (1922). These studies have been much extended by McBain and Kawakami (not yet published).

[5] See, for example, duPont Magazine, December (1923).

[6] We have used some of French manufacture and some made by the duPont Co.

Our special object was to develop this tool for detecting the presence of colloidal constituents in aqueous and, particularly, non-aqueous solutions of electrolytes, where anomalies in osmotic and electrical behavior are so frequent and yet where the possible presence of colloidal electrolytes has been overlooked in all reviews of the electrochemistry of non-aqueous systems. For this purpose it is essential to be satisfied that the membrane is much too coarse[7] to hold back any ordinary molecules, such as sucrose or anthracene. To avoid ambiguity in this respect we have refrained in general from using impregnated membranes.

The result is a demonstration that colloidal constituents are of very common occurrence in non-aqueous solutions of electrolytes that are usually regarded as quite simple, such as silver nitrate, silver bromate, or cadmium iodide.

The most striking result is that in aqueous solutions of certain electrolytes colloidal constituents are present. This is shown to be the case for the uni-univalent electrolyte potassium iodate which therefore is a colloidal electrolyte in aqueous solution.

Test of the Membrane with Known Crystalloidal Molecules[8]

It was found that known simple molecules, such as acetic acid, benzene, amyl alcohol, aniline and piperidine, pass freely through cellophane 600. In a previous communication[9] it was found that cellophane 600 has to be considerably thickened before it holds back sucrose at all. Further tests were made with solutions of naphthalene and of anthracene dissolved in benzene.

The membrane was made permeable to benzene by successive immersion in aqueous alcohol of several compositions up to 95 per cent alcohol which was then displaced by benzene. The original solution, the filtrate, and the residual solution above the membrane were each analyzed by measuring the refractive index by a Pulfrich refractometer, the results being compared with a previously established calibration scale. The data in Table I record experiments carried out by M. E. Laing McBain.

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[7] The bubble test of McBain and Kistler (Trans. Faraday Soc., **26**, 159 (1930)) showed that the larger pores are from 40-60 A in diameter.

[8] The very convenient form of ultrafilter used is that supplied by Vereinigung Gottinger Werke, Göttingen, with internal electrical stirring, and attachable directly to a cylinder of nitrogen. It is designed for pressures from one atmosphere up to 150 kilograms per square centimeter. All the chemicals (except where otherwise noted) were the purest supplied by Kahlbaum.

[9] McBain and Kistler: J. Gen. Physiol., **12**, 187 (1928).

TABLE I

Ultrafiltration of Anthracene and Naphthalene in Benzene

Substance	Expt.	Pressure	% Concentration of Filtrate	 Residue	Change in residue, %
Naphthalene	1	10 atms.	14.20	14.10	−0.10
	2	20 atms.	13.67	13.67	0.00
Anthracene	1	5 atms.	0.820	0.782	−0.038
	2	5 atms.	0.715	0.715	0.000

It is clear from Table I that filtration is not holding back any of these known molecules. Had either naphthalene or anthracene been held back by ultrafiltration, there would have been a positive increase in concentration of the residue and hence necessarily a corresponding loss in the ultrafiltrate. It is interesting to note that in an earlier experiment with a sample of "anthracene," which was subsequently found to be very impure, colloidal impurities were concentrated in the residue.

Proof that Colloidal Constituents are present in Solutions of Silver Bromate in Diethylamine

McBain and Coleman in 1913-1914[10] carried through a careful study of solutions of silver bromate in diethylamine. The boiling points and lowerings of vapour pressure calculated in the usual (erroneous) manner indicate association instead of dissociation ranging from 3.4 fold in 0.89 N_w to 2.04 fold in 1.64 N_w solutions. The conductivity shows a maximum of 2.64 mhos at 1.7 N_w, nearly disappearing on dilution to 0.07 N_w. Such behavior is not infrequent in non-aqueous solutions and bears some resemblance to that of aqueous solutions of the soaps which are now accepted as the best studied type of colloidal electrolytes.

For the ultrafiltration experiments,[11] diethylamine (Eastman Kodak Co.) was distilled and that fraction distilling within 0.2° was used. The silver bromate was made by double decomposition of potassium bromate and silver nitrate, the finely crystalline precipitate being washed thoroughly with distilled water and dried at 100°.

The temperature gradient of the solubility curve is particularly steep. Thus at 20°C the saturated solution has a concentration of 0.115N_w, while at 32° the concentration has risen to 1.3N_w. At 40° Coleman obtained a 3.12 N_w solution. This is like some of the soaps. If the solvent is distilled after use or after contact with the membrane, the solubility of silver bromate is still higher, moisture perhaps accounting for the increase. All these solutions showed a brown precipitate on longer standing, due probably to silver oxide since its amount was proportional to the moisture content.

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[10] Not yet published.

[11] The ultrafilter was heavily plated with silver before use.

Analysis of silver bromate in the presence of diethylamine presents difficulties, since the latter makes it impossible either to determine the silver by the Vollhard method or to determine the bromate ion by oxidation of hydriodic acid and final titration with sodium thiosulfate. The following method gave good results. The solution is added to about 200 cc of water, made alkaline with sodium hydroxide and boiled for about one-half hour. The diethylamine is completely driven off and the silver is precipitated as flocculent Ag_2O which is titrated with ammonium thiocyanate after solution in dilute nitric acid. The bromate ion is reduced with hydriodic acid and the iodine titrated. This method not only gives a double check but shows whether there is a preferential concentration of either ion during the ultrafiltration.

The following table gives the quantitative results obtained after standardizing the method of analysis.

TABLE II

Ultrafiltration of Silver Bromate in Diethylamine

Concentration filtered	Temperature	Increase in concentration of residue
0.130 N_w	20°	0.0%
0.960 N_w	40°	12.8%
1.29 N_w	32°	28.1%*
1.37 N_w†	20°	21.0%

* Concentration of filtrate 1.00 N_w, of residue 1.65 N_w.
† Moisture present.

It will be seen from Table II that the higher the concentration of the solution, the greater is the proportion of colloid as shown by the per cent increase in the original solution. This is to be expected from Coleman's data and from analogy with soap solutions which are colloidal electrolytes but on sufficient dilution become simple, ordinary electrolytes.

Proof that Colloidal Constituents are present in Solutions of Silver Nitrate in Piperidine

Lincoln[12] found that solutions of silver nitrate in piperidine show a continuous decrease in equivalent conductivity with dilution. The following table gives the data obtained by ultrafiltering silver nitrate solutions in piperidine through cellophane first swollen in piperidine rather than in water, this treatment resulting in the same rate of filtration.

TABLE III

Ultrafiltration of Silver Nitrate in Piperidine

Original Concentration	Membrane	Increase in residue
0.065 N_w	300*	10%
0.120 N_w	600	29%
0.246 N_w	400	40%

* Cellophane 300 is more porous than cellophane 600.

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[12] J. Phys. Chem., 3, 470 (1899).

The fact that the percentage of silver nitrate retained upon filtration increases rapidly with increase in concentration of the solution filtered again suggests that in the more concentrated solutions the frequency of larger molecular aggregates is much greater, as would be expected.

The results of further exploration are collected in Table IV which is followed by any necessary supplementary details.

TABLE IV

Ultrafiltration Data for Substances in Non-Aqueous and Aqueous Solution

Solute	Solvent	Original Conc.	Membrane	Per cent Increase in residue
Ammonium iodide	Aniline	0.28 N_w	600	11.4
Barium perchlorate	Amyl alcohol	0.47 N_w	600	13.0
Cadmium iodide	Amyl alcohol	1.083 N_w	600	3.6
Cadmium iodide	Amyl alcohol	1.083 N_w	$600^{\dagger}$	44.0
Cadmium iodide	Ethyl alcohol	2.76 N_w	$600^{\dagger}$	* *
Potassium acetate	Acetic acid	1.34 N_w	1200	9.0
Pyridine	Acetic acid	10%	600	10.0
Sodium acetate	50% acetic acid	8%	600	3.0
Potassium iodate	Water	0.35 N_w	$2400^{\ddagger}$	12.0
Potassium iodate	Water	0.333 N_w	1800	16.8^{ϕ}
Potassium iodate	Water	0.333 N_w	600	7.3^{ϕ}
Potassium iodate	Water	0.333 N_w	600	13.6^{ϕ}

Qualitative experiments with acetic acid in isoamyl alcohol, copper acetate in amyl alcohol and mercuric iodide in benzene are not reported since special reasons in each case rendered them inconclusive.

† Swollen in aqueous ethyl alcohol.

** Residue not analyzed; filtrate was 1.02 N_w.

‡ Reinforced.

ϕ Experiments by Miss W. L. McClatchie About four-fifths was filtered before analysis. The increase in concentration of the residue was, of course, accompanied by a corresponding decrease in concentration of the filtrate. The ultrafilter used was heavily silver plated throughout. Analysis was made by titration with thiosulfate after addition of potassium iodide.

In the experiments with ammonium iodide in aniline there was much difficulty due to polymerization, or possibly to reaction with the material of the filter, since the residue always developed a brownish precipitate. However, the satisfactory result here recorded was obtained after silver plating the filter. Then there was no residue or decoloration, but after long standing, the silver plating is loosened. The increase in concentration observed, ascribable to colloid constituents, accords well with the observation of Sachanov[13] who obtained a minimum in equivalent conductivity at approximately 0.12 N.

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[13] Bull. Acad. Imp. Sci., St. Petersburg, p. 106 (1913).

The results for barium perchlorate in amyl alcohol show a fair proportion of colloid, though there are no conductivity data for comparison. Migration experiments by Hittorf, using cadmium iodide in amyl alcohol, showed a negative migration of cadmium that was so pronounced that the migration number of the iodine attained the extraordinary value, 2.3. Mere complex ions would hardly be expected to give so large a value, and it would appear that we have here a case analogous to that of soap curd in which the anion migration number ranges from 2 to 4 and is explained by the presence of large amounts of neutral colloid. These experiments show very definite evidence of the presence of colloid.

For cadmium iodide in ethyl alcohol, the ultrafiltration, though not complete, supports the suggestion of colloid complexes indicated by the minimum conductivity between 0.01 and 0.02 N as measured by Jones and Mahin.[14]

The filtration of potassium acetate in acetic acid was unusually slow, 10 hours being required for 7 cc of filtrate to collect at a pressure of 75 atmospheres. However, this was possibly due to the extreme fineness of the membrane, number 1200 being used. The increase in concentration is again paralleled by an anomalous conductivity curve. Völmer[15] found a pronounced maximum and minimum in the conductivity curve for this system, potassium acetate and acetic acid.

Pyridine in acetic acid exhibits both a maximum and a minimum in its equivalent conductivity curve.[13] In the ultrafiltration experiment recorded, some difficulty in analysis was experienced, for the pyridine acetate seemed to act as a buffer in the titration with sodium hydroxide. Jones and Carroll[16] found that the equivalent conductivity of sodium acetate in aqueous acetic acid solutions exhibits a minimum. The shape of the curve is greatly influenced by the percentage of acid, showing the greatest abnormality at 50 per cent acid. The solutions were analyzed by density, and there is again an increase in concentration of the residue by filtration.

Potassium Iodate as a Colloidal Electrolyte in Water

0.333 N_w potassium iodate in water when filtered at 50 atmospheres pressure through an unthickened cellophane membrane (number 1800) gave a 16.8 per cent increase in concentration in the residue and a corresponding decrease in the filtrate. Cellophane number 600 exhibited the same unmistakable effect. This confirms the similar result obtained with a thickened membrane and leads to the remarkable conclusion that aqueous potassium iodate contains colloidal constituents.

It is well known (compare International Critical Tables) that, whereas aqueous solutions of iodic acid exhibit excellent conductivity, they give a lowering of freezing point which is far less than that of such an electrolyte as hydrochloric acid. This would be characteristic of a colloidal electrolyte, but no one has cared to give this interpretation to the data, and the matter has not been further tested. Jones and Bury,[17] and Grindley and Bury,[18] have concluded that micelle formation occurs in aqueous solutions of butyric acid. McBain and Van Rysselberge[19] have shown that complex ions are of normal occurrence in aqueous solutions of electrolytes, but this new result from ultrafiltration points to further unsuspected constituents. Needless to say, such results are incompatible with any assumption of complete dissociation of electrolytes save in extreme dilution.

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[14] Z. physik. Chem., **69**, 389 (1909).

[15] Z. physik. Chem., **29**, 187 (1899).

[16] Am. Chem. J., **32**, 542 (1904).

Summary

It is shown that cellophane provides a membrane which holds back all but the smallest colloidal particles and allows all known simple molecules to pass through. It serves as a test to show that colloidal constituents are commonly present in the numerous non-aqueous solutions of electrolytes, such as silver nitrate, ammonium iodide, silver bromate, cadmium iodide, etc., which exhibit anomalies in electrical conductivity and osmotic behavior, and may even occur in aqueous solutions of electrolytes such as potassium iodate. It is pointed out that these membranes may be thickened as desired until they hold back large molecules and ions, such as sucrose and sodium or potassium chlorides, while still allowing the smaller molecules to pass through.

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[17] Phil. Mag., (7), **4**, 841 (1927)
[18] J. Chem. Soc., 679 (1929).
[19] J. Am. Chem. Soc., **50**, 3009 (1928); **52**, 2336 (1930).

A STUDY OF THE BLOCKING EFFECT OF MEMBRANES

BY G. H. BISHOP, FRANK URBAN, AND H. L. WHITE

In connection with a study of the filtration process through the glomerular membrane of the kidney by one of us occasion arose to investigate certain aspects of filtration through supposedly less complex membranes, as cellophane. The results of these experiments being still too complex for analysis, we have been led to an examination of the flow of solutions through glass capillaries of 0.035 to 0.150 mm inside diameter, varying also in length and degree of taper. We believe that certain deviations in our results from the conventional law for the value of streaming potentials may assist in the interpretation of corresponding deviations from simplicity in the behavior of cellophane membranes. It is barely possible that this may in turn contribute to an understanding of the biological process.

Cellophane membranes were tied over thistle tubes and sealed on with collodion, and the volume flow read by means of a microscope on the capillary stem. Volume change due to slow stretch of the membrane was checked by supporting the membranes in certain experiments with perforated plates, and by forming collodion or cellulose acetate membranes on alundum disks. Tapered or straight capillaries were made by drawing out very heavy walled pyrex capillary tubing and employing either the uniform middle section or the rapidly tapering end. These were sealed into larger tubes after measuring the diameters at each end; the outer tube was allowed to fall in upon the middle of the section of capillary used without distorting the lumen, as seen in Fig. 3, U.

Calomel electrodes sealed into the system allowed voltage readings to be taken, and other electrodes permitted application of current across the system. Readings were made by connecting the apparatus in series with a two m.f. condenser to the EMF leads of a Leeds and Northrup type K potentiometer, so that at balance the condenser was uncharged. The condenser charge was detected by a galvanometer of 10^{-10} amp sensitivity used ballistically, 0.1 millivolt discharged from the condenser giving a detectable deflection.[1] Potentials can be read significantly when the source measured has a resistance of 10^9 ohms, with adequate insulation and allowing sufficient time for charging the condenser. Pressure from the air line was regulated by escape from a side tube dipping into an iron pipe A filled with mercury, to an adjustable depth, and read on a mercury manometer B (Fig. 3). All units of the apparatus were mounted separately on ¼ inch plate glass.

Results. When water or dilute KCl solution (0.0005 to 0.005 molar) is forced through cellophane membranes under pressure of 80 mm Hg or less, the streaming potential cannot be detected (less than 0.1 mv). Filtration commences at a maximum rate when the pressure is applied and in the course of 15 minutes to 1 hour may fall off to as low as ten per cent of the initial rate. The results of such an experiment are shown in Fig. 1, curve 1, where the slope of the curve represents the rate of filtration. Such blocking has been observed before by various workers on different membranes,[2] With higher salt concentrations this blocking decreases; also, it was not seen when a solution of 0.01 gm $ThCl_4$ per liter was filtered through the same membrane, (Fig. 1, curve 2). Electroendosmose without pressure exhibits the same phenomena, with similar time relations. Application of a constant current after equilibrium conditions have been obtained under pressure (two hours' filtration) give the same result. With pressure alone, when this is removed the flow reverses; if only reduced the flow may first reverse and then proceed in the previous direction. The same applies to application of current alone without pressure, thus indicating that stretch of the membrane is not a factor. Upon cessation of applied current, a residual (polarization) EMF persists, and its disappearance has a time course closely parallel to that of the accompanying filtration. It thus appears that the blocking of filtration through these membranes may be correlated with the electrical phenomena of the nature of polarization which are associated with electroendosmose; the difficulty of such an interpretation arises from our inability to detect a potential across the membrane under filtration pressure which should account for the blocking of the filtration process.

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[1] Bishop: Proc. Soc. Expt. Biol. Med., **21**, 260 2 (1930).

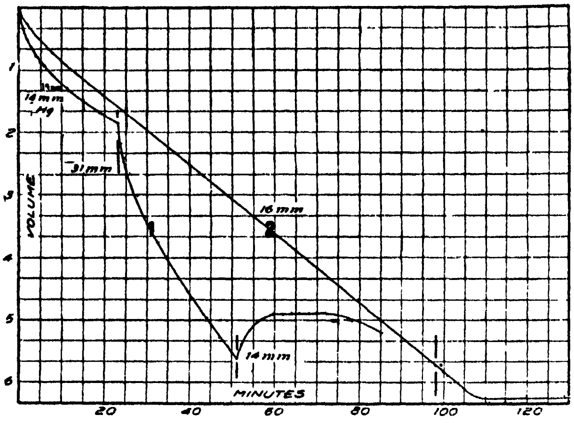

FIG. 1

It seemed possible that the two phenomena, the gradual falling off in the rate of filtration and the absence of a measurable potential difference (streaming potential) across the membrane might have a common explanation in differences in the behavior of the electrical processes taking place in the various pores of the membrane. Thus, if for any reason the streaming potential between the ends of the pore AB was greater or developed more rapidly than with the pore CD, a return circuit would be set up through CD. Fig. 2. The point D being negative to the point B, a current would flow as indicated by the curved arrow, constituting essentially a Dolezalek's ring circuit. The plus sign below and the minus sign above the membrane indicate the potential difference which would be set up across the membrane provided the streaming potentials were allowed to develop unhindered. The short circuit through the relatively inactive pore CD would oppose electrosmotically the flow of solution due to the pressure head, resulting in an apparent falling off in the rate of mechanical filtration, and would at the same time discharge the potential difference across the membrane. This hypothesis, offered in explanation of both the falling off in filtration rate and the absence of a measurable potential difference across the membrane, can be defended only if it can be demonstrated that some factor or factors as, for instance, differences in size or shape, *ceteris paribus*, can result in differences in the electrical activity of various capillaries, *i.e.*, can result in a lesser magnitude or a slower development of the streaming potentials of some capillaries as compared with others. Since it is obviously impossible to investigate the behavior of the individual pores in a cellophane membrane we have used glass capillaries as models of these pores.

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[2] **Brukner**: Z. Ver. deutsch. Zucker Ind., **76**, 3 (1926); Simon and Neth: Z. anorg. allgem. Chem., **168**, 221 (1928); "Membranefilter, Cella und Ultrafilter," 20 (1920); Manegold and **Hofmann**: Kolloid-Z., **50**, 22 (1930).

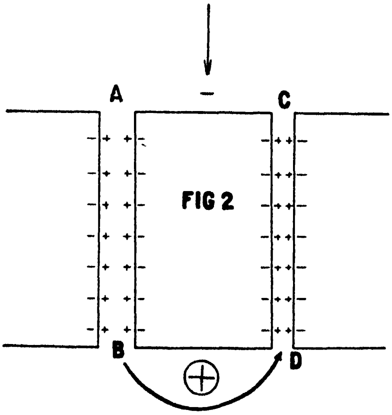
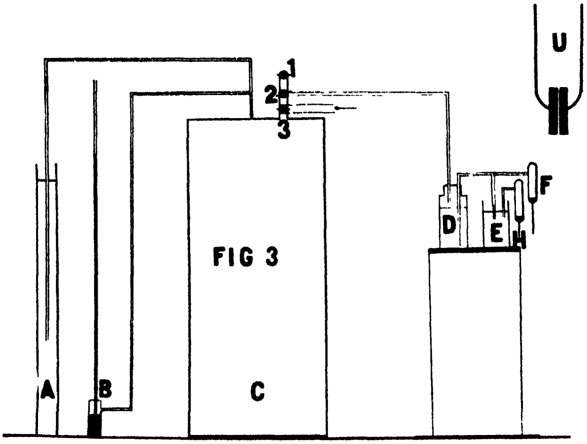


FIG 2

The apparatus diagrammed in Fig. 3 was used. In some of the experiments a single capillary dipped into a beaker E, as shown in the figure, in others the outlet tube from the bottle D was branched and bore on each of its branches a capillary dipping into its own beaker. Great care was taken to prevent contamination of the 0.0005 molar KCl in the capillaries by diffusion of the 0.05 molar KCl in the calomel electrodes, H and F. In all our experiments on glass capillaries 0.0005 molar KCl has been used.

The results of an experiment with a pair of capillaries are given in Fig. 4. The smaller capillary, curve 2, had an inside diameter at the tip of 0.075 mm and passed 0.6 cc of solution per minute at 40 cm Hg pressure; the larger, curve 1, had a diameter of 0.125 mm at the tip and passed 7.2 cc of solution per minute; both of them tapered rapidly to the tip. Thirty runs made over a period of 10 consecutive days at pressures ranging from 20 to 60 cm Hg invariably showed a higher final streaming potential for the larger capillary. Furthermore, the development of the potential was much slower with the small than with the large; the potential of the larger capillary had usually practically reached its maximum before that of the smaller began to show a significant rise. It is obvious that if both these capillaries had had their tips dipping into the same container, as is of course the case for all the pores traversing a filtering membrane, the conditions diagrammed in Fig. 2 would be realized. In another set of experiments the smaller capillary showed the lower potential at low pressure, up to 40 cm Hg, while at pressures above 40 and up to 80 cm the potential of the smaller capillary was the greater.

In another experiment the effect on the streaming potential of breaking off successive fragments or a tapering capillary was investigated, the pressure remaining constant at 60 cm Hg. The results are shown in Fig. 5; the data are plotted semilogarithmically merely for convenience. It will be seen that at first the potential rises as the rate of flow, due to decreased resistance, increases; with further increase in the rate of flow the potential falls. This experiment is complicated by the fact that the shape as well as the size of the capillary is being changed. In another experiment with a straight capillary (inside diameter 0.040 mm) 5 cm long the potential was unchanged on reducing the length by one half; the rate of flow was doubled. We believe that the shape (whether straight or tapering) as well as the diameter of capillaries is a factor in determining the magnitude of the streaming potential and its rate of development. The change of potential with time in a single capillary suggests a counter force analogous to a polarization counter EMF. In a tapered capillary there should be forces of different magnitude at the two ends of the capillary. The rise to a maximum with subsequent marked fall shown by the potentials of such capillaries resembles the curve of charge of two condensers of different sizes in series, with suitable leak circuits, such shunted condensers being satisfactory models for polarizable mechanisms[3]. An extended consideration of this question cannot be entered into in the present communication.



In an effort to evaluate the factor of capillary diameter alone, three untapered single capillaries were taken, having inside diameters of 0.040,

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[3] Bishop: Am. J. Physiol., 85, 417 (1928).

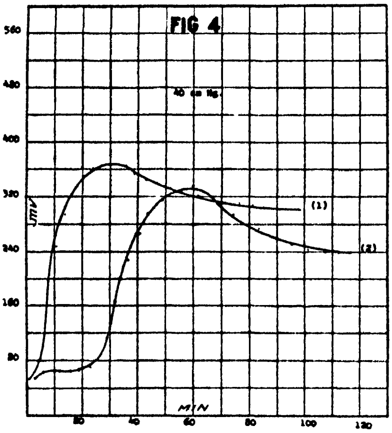
FIG 4

0.080 and 0.125 mm, respectively; the first was 5 cm long, the others 1 cm long. The fact that one of these capillaries was longer than the others was not considered as invalidating a comparison on the basis of differences in diameter, since the results of a single experiment, referred to above indicated that for straight capillaries the streaming potential was independent of the length. It would seem at first thought a simple matter to take three capillaries of different diameters and compare their streaming potentials. The matter is complicated, however, by the fact that the streaming potential of one and the same capillary has, in many of our experiments, fallen off from day to day. This has not always been the case; thus, with one straight capillary of 0.035 mm inside diameter the streaming potential at 60 cm Hg stayed between 735 and 750 millivolts for 17 consecutive days. In other experiments, where equally strenuous efforts were made to keep conditions constant, the potential showed a progressive fall from day to day. This was the case with all three of the capillaries under consideration here. It was arbitrarily decided to take as the basis of comparison the maximum potential shown by each capillary on

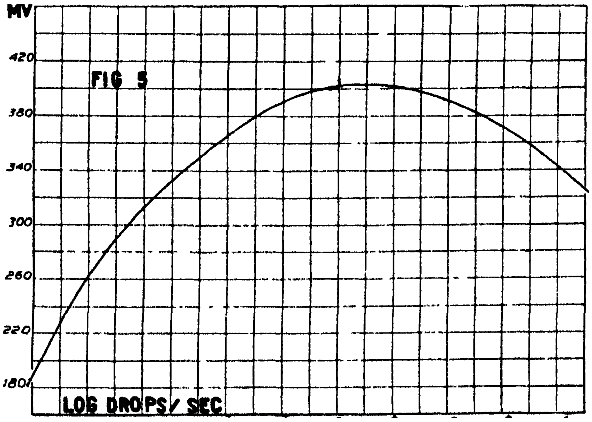
FIG 5

the second day of its use. It was found that the 0.040 mm capillary showed a potential of 392 mv, attained 188 minutes after the pressure of 60 cm Hg was applied, the 0.080 mm capillary showed 681 mv, attained after 190 minutes and the 0.125 mm showed 333 mv after 64 minutes. From this series alone one might conclude that there is an optimum diameter for the development of a stream potential, lying between 0.040 and 0.125 mm. We are not ready to state, however, that this is the case; we can only say that there appears to be a relation between capillary diameter and stream potential but it apparently is not a simple one. It may be noted that earlier workers who have investigated the possibility of an influence of capillary diameter on streaming potential have worked with quite large capillaries. Dorn[4] used capillaries ranging from 0.252 to 4.113 mm in diameter. Their failure to find a relation between capillary diameter and streaming potential may merely mean that the sizes they used were above the range where diameter influences potential, except in so far, as noted by Dorn, the excessively large diameters bring about a departure from Poiseuille's law.

It is evident that the matter of variation in streaming potential of a given capillary from day to day demands further investigation. This has been noted since the earliest reports on the subject; no more definite explanations have been advanced than those of Helmholtz[5] that a part of the active surface of the glass may undergo dissolution, that adhering foreign substances may gradually be washed away or that the negative component of the double layer may penetrate more deeply into the glass, bringing about a redistribution of the pore charge with a resultant change in the steaming potential. Grumbach[6] and Kruyt[7] report only a slight falling off during ten days. In many of our experiments the extent of fall is greater than we have found reported by previous workers. The possibility that this might be due to contamination of the capillaries with the 0.05 molar KCl from the electrodes was considered. We believe for two reasons that this is not a factor. In the first place, some of our capillaries have kept a practically constant potential for many days, although the opportunities for contamination were the same as with those which showed the falls. In the second place, the possibility has been tested directly as follows. The beaker E (Fig. 3) was filled with 0.05 molar KCl at a time when the level of solution in the bottle D was 5 cm below the level in the beaker E; the system was allowed to stand for one hour. The streaming potential before the beaker was filled with 0.05 molar KCl, *i.e.*, when it was filled as usually with 0.0005 molar KCl, had remained steadily at 362 mv for over 30 minutes, the pressure being 60 cm Hg. After the capillary had had its tip in the 0.05 molar KCl with this strong solution siphoning up into the capillary for an hour, the 0.05 molar was replaced by 0.0005 molar KCl. The first reading, made one minute after the replacement, was 65 mv, 2 minutes later was 310 and 2 minutes later was 357. It thus appears that the potential is restored even after a known contamination with relatively concentrated KCl solution as soon as the latter is swept out of the capillary. We do not yet know the cause of these drops in potential; they are not due to mechanical plugging of the capillary by foreign particles, as has been established by determinations of the rate of flow.

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[4] Wied. Ann., **9**, 513 (1880).
[5] Wied Ann., **7**, 344 (1879).
[6] Ann. Chim. Phys., **24**, 433 (1911).
[7] Kolloid Z., **22**, 93 (1918).

A systematic investigation of several of the points considered here is in progress but is far from being complete. The exact roles played by differences in diameter and shape and by "spontaneous" changes in the nature of the capillary wall in determining differences in the stream potentials of various capillaries are at present not at all clear. It may again be pointed out, however, that for the statement in a preliminary form of the hypothesis proposed here a complete knowledge of the mechanisms involved is not essential. The conditions diagrammed in Fig. 2 will be realized if for any reason the streaming potential of certain capillaries or pores is different from that of others, either as to magnitude or to rate of development. Even though the pore CD has the potentiality of attaining ultimately a streaming potential equal to that of AB it will not have a chance to develop it if the beginning of its development is tardy. For the return circuit through CD, by opposing electrosmotically the flow due to the head of pressure prevents the normal downward passage of liquid through CD and thus deprives CD of an opportunity to develop any streaming potential. We have established that various capillaries made from the same piece of glass, subjected to the same treatment, left for the same periods of time, having the same solutions forced through them at the same pressures may exhibit significant differences in streaming potential; regardless of the reasons for the differences, the fact constitutes a substantial support to the hypothesis. Since it is only reasonable to assume that there are great variations in the shapes and sizes of the pores traversing a membrane and not unreasonable to assume, in view of experiences with "uniform" sample of glass capillaries, that the ζ potential is not the same in all the pores of the membrane, it seems probable that the conditions established for glass capillaries and diagrammed in Fig. 2 obtain in filtering membranes.

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THE DENATURATION OF ALBUMIN*

BY WILDER D. BANCROFT AND J. E. RUTZLER, JR.

1. Denaturation by Heat

Man is incurably empirical. When a given experiment fails to produce the expected result, he says it will not work. Whereas, were he neither empirical nor dogmatic he would say that it does not work.

When egg albumin or egg white, as the case may be, is heated to a certain temperature, coagulation of the suspended particles takes place. Because people, in the past, failed to repeptize the gel so formed, it has been tacitly assumed that it cannot be restored chemically unaltered, at least, to the original colloidal state. Some profound change has been held responsible for this failure of the albumin to repeptize. This apparent set of circumstances left an opportunity open to coin a word; the term "denaturation" or "denaturization" resulted inevitably.

Much has been written about "denaturation", for instance, the following:[1] "One of the most characteristic properties of the albumins is the physical instability of their solutions and their marked tendency to revert to a solid or semi-solid state. This change may be effected by apparently trivial factors, such as evaporation, contact with porous substances, etc. In this respect also the albumins behave very much like the inorganic colloids. This change (irreversible coagulation) can be brought about at once by the application of heat, and it is important to note that *all true native albumins can be coagulated* in this manner. After coagulation their solution can only be effected by influences which lead to their more or less extensive destruction. They have lost those physical properties which characterized them individually as albumins; they are permanently *denaturized*, as Neumeister expresses it."

On page 32, Simon continues: "Coagulation is not an essential phase of denaturization. Denaturization may indeed become manifest by the non-occurrence of coagulation. Denaturized and coagulated albumins can only be brought into solution by means which will at the same time produce integral changes in their composition, viz: by means of proteolytic ferments, dilute mineral acids or alkalies, concentrated organic acids under the application of heat, etc.

"The nature of the process which determines denaturization is possibly a primary cleavage. Nothing certain, however, is known."

It would seem from this quotation that denaturation is a process occult and more or less unintelligible.

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* This work is part of the programme now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Simon: "Physiological Chemistry," 30 (1904).

Writing of "Denaturation and Coagulation", Miss Lloyd[1] says: "Coagulation is a physical condition, and by suitable means coagula can be redispersed or dissolved. The solution of coagulated protein, however, differs very definitely from that of the original material from which it came. Coagulation is not in itself an irreversible process, but in all cases is preceded by an *irreversible chemical change in the protein known as denaturation.*[2]

"Under the heading of 'denaturation' can be included a number of reactions, the common features of which are a complete loss of solubility in water and in dilute salt solutions. Denatured proteins, however, are readily dissolved in dilute acids or alkalis, giving viscous colloidal solutions which react towards electrolytes as if they were of the suspensoid type rather than the emulsoid type characteristic of normal proteins. The change involved in denaturation seems to be a structural alteration in the protein molecule, which leads to a re-arrangement of the linkages in the molecule, but not an actual degradation. This change is accompanied by a complete loss of the power of swelling by the imbibition of water. . . . Proteins can be denatured by strong acids or alkalies, by salts of the heavy metals, by heat, by light, by mechanical agitation, by pressure or adsorption on a surface, and by the action of alcohol or acetone. The interrelation between different types of denatured proteins has not yet been worked out.' "

On page 229 Miss Lloyd continues: "The commonest example of this [heat denaturation] is, of course, the setting of the white of an egg which takes place on boiling. Denaturation and coagulation are both influenced by temperature, time, the reaction of the solution, the presence of water and by the nature and concentration of the electrolytes present; but the effect of these factors is different for each of the two processes."

Bechhold[3] also makes the point that when proteins are denatured they lose their capacity to swell. On page 163, Bechhold makes the definite statement that, "reversible coagulation is purely a salting out, whereas one must assume a chemical change with irreversible coagulation."

Young[4] maintains that denaturation is a primary chemical change.

Anson and Mirsky[5] make the statement that, "denaturation is not a general disintegration of the native protein." In a second paper the authors[6] come to the conclusion that denaturation and its reversal are very obscure chemical changes.

We find Robertson[7] on record as follows: ". . . which leads to the apparently irreversible character of the process (dehydrating proteins by heat); *apparently* and not actually irreversible because, as Corin and Ansiaux[8] have shown, if a solution of protein be cooled and vigorously shaken just as the first traces of heat coagulation appear, the incipient coagula will again pass into solution. The apparent irreversibility of the later stages of heat-coagulation is probably attributable to the high internal friction of the floccula which are formed, leading to extremely slow molecular movement and the introduction of a time element of very considerable magnitude."

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[1] "Chemistry of the Proteins," 228 (1926).

[2] Hardy: J. Physiol., **24**, 158 (1899).

[3] Bechhold: "Die Kolloide in Biologie und Medizin," 161 (1929)

[4] Proc. Roy. Soc., **93B**, 235 (1922).

[5] J. Gen. Physiol., **13** II, 121 (1929).

[6] J. Gen. Physiol., **13** II, 133 (1929).

[7] "The Physical Chemistry of the Proteins," 308, 309 (1918).

[8] Bull. Acad. roy. Belg., (3) **21**, 321, 345 (1891).

Cohnheim[1] says that albumin cannot be put back into solution without extensive changes and splitting; it is permanently denatured.

The denaturation of serum albumin solution by heat can be retarded by adding sucrose or glycerol to the system.[2] The physico-chemical properties of the native proteins are left more or less unchanged as a result. The protective action of the glycerol was found to be less than that of the sucrose. Further, with sufficient concentration of sucrose, rabbit serum proteins were found to be completely thermostable at 62°; while egg albumin, under like conditions, was thermo-stable at 75°.

Albumin is prevented from coagulating[3] even in boiling water by the presence of starch. Coagulated egg albumin was found to redissolve when heated to 148° with a small quantity of water.

Chick,[4] working with pseudo-globulin, derived from horse serum, makes the statement that denaturation cannot be identified with any chemical changes in the material; whereas we find that Wu[5] concludes that the essential step in denaturation is a hydrolytic fission of the protein, and the essential step in coagulation is molecular condensation. Earlier Chick and Martin[6] maintained that the fact that the hydrogen ion concentration diminishes after heat coagulation points to the view that denaturation is a chemical change.

"It is not at present easy to form a satisfactory theory of denaturation," are the words Miss Lloyd[7] uses in launching a discussion of the theories of denaturation. The author then mentions three prevalent theories, the opening up of internal anhydride rings, the closing of rings with the consequent formation of internal anhydrides, and hydrolytic cleavage, none of which are adequate to explain all the facts.

From this short review it becomes obvious that the behavior of albumin, as a result of which it supposedly becomes either irreversibly coagulated or chemically changed, is not clearly understood. People are at variance as to the mechanism; and cause and effect are sometimes apparently confused. The whole problem has been approached from the viewpoint of true solutions, or colloidal ions, or amphoteric electrolytes. The problem has not been considered logically from a strictly colloid chemical viewpoint.

[1] "Chemie der Eiweisskorper," (1911).

[2] Beilinsson: Biochem. Z., **213**, 399 (1929).

[3] Kingzett: "Animal Chemistry," 380 (1878).

[4] Biochem. J., **8**, 404 (1914).

[5] H. Wu: Chinese J. Physiol., **3**, 1 (1929); Chem. Abs., **23**, 4952 (1929).

[6] J. Physiol., **40**, 404 (1910).

[7] "Chemistry of the Proteins," 243 (1926).

Bancroft,[1] in discussing the effect of electrolytes on albumin, says: "In other words, we will give up, for the time being, the dogma that albumin is an amphoteric electrolyte." Further, "the precipitation of a colloid is always reversible in case no coalescence or agglomeration takes place, because one of the standard methods of preparing a colloidal solution is to wash out the excess of the precipitating agent. Now the more strongly the precipitating agent is adsorbed, the harder it is to wash it out and consequently the more nearly irreversible the precipitation is."

Electrolyte-free albumin is said to be very stable toward the action of heat,[2] although Pauli[3] disputes this finding. Also, it is well known, that electrolyte-free albumin does not coagulate on standing. Concerning this Bancroft says: "The only way that I see to account for the stability of the electrolyte-free albumin is to postulate that in the absence of salts the peptizing action of water is enough to keep the albumin in colloidal solution.

"It does seem to me, however, that it will be an easier task to account for the properties of electrolyte-free albumin on the basis of varying adsorption than on the basis of an amphoteric electrolyte".

Wo. Ostwald[4] takes a step in the right direction when he says: "Albumin sols are usually amphoteric, that is, they must be either positively or negatively charged, depending upon certain conditions," although the way the word amphoteric is used is somewhat unfortunate.

Kruyt[5] is quite positive in his discussion of proteins as colloids. "There is, however, a special reason which has led many investigators to look upon emulsoids as molecularly dispersed systems, more particularly, as electrolyte solutions; this is the fact that a great many properties of protein solutions may be explained by considering these solutions as systems of *amphoteric electrolytes*. It may be pointed out at this place that a discussion of emulsoids in terms of ionically dispersed systems must necessarily conflict with typically colloidal properties of these systems.

"The main criticism that can be raised against the concept of the electrolyte nature of protein solutions lies in the fact that the division of colloids into suspensoids and emulsoids would then be without continuity. In other words, we should have to ascribe to colloid chemistry a dualistic line of reasoning which is highly unsatisfactory. Whereas, for instance, the electrical properties of suspensoids are to be explained by means of the electro-adsorptive phenomena of the peptizing ions which divide themselves between the particles and the medium . . ., we should have to consider for protein solutions an ionic equilibrium of one single kind of molecules dissociated into ions, the degree of dissociation being governed by Ostwald's dilution law."

Denaturation, in review, is defined as the irreversible precipitation of a protein sol. Likewise, coagulation is defined as the reversible precipitation of a protein sol. There is an experiment which apparently illustrates this difference between denaturation and coagulation. Pauli and Handovsky[1] boiled an egg albumin system which was 2-normal in respect to potassium thiocyanate. There was no coagulation. A control system and a portion of the treated sol were dialyzed against running water. The control system remained clear; whilst, unfortunately, there was extensive flocculation in the treated sol. The boiled, undialyzed system containing potassium thiocyanate is considered to be denatured but not coagulated.

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[1] J. Phys. Chem., **19**, 349 (1915).

[2] Schmidt: Pflügers Archiv, **8**, 75 (1874); Heynsius: **9**, 514.

[3] Beitr. chem. Physiol., **10**, 53 (1907).

[4] "Practical Colloid Chemistry," 151 (1924).

[5] "Colloids," 178, 179 (1927).

Denatured serum albumin has been reversed by Spiegel-Adolf.[2] The serum albumin was treated with dilute sodium hydroxide solution. "The experiments were carried out thus: Varying quantities of the same heat denatured albumin were dissolved in 100 cc. of 0.01 N NaOH in exactly the same way. It then appeared that the absolute content of the protein of the resulting solutions decreased with the decreasing quantity of the proteins employed, while a constantly decreasing residue of protein remained undissolved. If these liquids were electrodialyzed, the quantity of protein remaining in solution was found to decrease with a decrease in the initial quantity of heat-denatured protein used, and finally to disappear. That is, from the solution of 0.5 gram of heat-denatured albumin in 100 cc. of 0.01 N NaOH, there results a protein solution which is quantitatively precipitated on electrodialysis. There exist, therefore, two limiting cases, within which there are continuous transitions. With a sufficiently large excess of protein, we get only water-soluble protein; with a correspondingly large excess of alkali, only a water-insoluble protein." The water soluble protein was obtained by dissolving 4 grams of serum albumin in 100 cc. of 0.01 N NaOH.

"From this physico-chemical evidence, the product in question (the water-soluble protein) is not distinguishable from true albumin.

"In order, however, to try a further criterion for the characterization of protein X, the highly sensitive immuno-biological methods were employed. The precipitin method was selected." The experimental results show that both horse serum-albumin and the electrodialyzed sample (4 grams of protein dissolved in 100 cc. of 0.01 N NaOH) behave as antigens toward the precipitin up to a dilution of one part of protein to one hundred thousand parts of physiological salt solution. The negative result of the control test demonstrates the specificity of the reaction."

The author then summarizes, p. 311: "Accordingly no essential difference is demonstrable between protein X and its parent material (a true serum albumin) by the physico-chemical and immuno-biological methods here employed. The agreement is so close that, provided no new experimental results arise to contradict it, we are forced to admit an actual identity of the two proteins. Such an identification, however, would imply that the changes produced by heat had been made chemically reversible by the treatment given the heat-coagulated albumin."

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[1] Bechhold: "Die Kolloide in Biologie und Medizin," 170 (1929).

[2] Alexander: "Colloid Chemistry," **2**, 309 (1928).

In an attempt to explain the chemical changes which have supposedly taken place, the author says on page 313: "The demonstration that the changes brought about by heat can be reversed by small amounts of alkali or acid, supports the view that ring closure accompanies the heat-change. For, while the action of these added substances, which persists even after their electrodialytic removal, can be interpreted as an hydrolysis, there might possibly have been involved a breaking down of a pre-existing ring structure. On the other hand, it is not obvious how any previously occurring hydrolysis can be completely reversed by an added substance which itself is known to aid hydrolysis. The above findings seem to strengthen the theory that the change appearing upon heat-denaturation of the proteins depends upon a ring closure of the groups involved."

The reversal of denaturation is obviously a paradox. It can be accounted for in two ways. In the first place, the experimental results of Spiegel-Adolf can be discounted. This seems to be highly improbable.

Refusing to challenge these results brings up the question as to whether the term denaturation is really accurate or not. This will be taken up later.

Wilhelm[1] predicted, in 1927, that it should be possible, under the correct conditions, to reverse denaturation. In a later paper[2] he made good on his prediction and reversed heat-denatured serum albumin. The coagulated albumin was prepared by electrodialysis in a hot water bath, or over a free flame. The gel was repeptized by heating it in boiling water containing a definite amount of salt. The salts used were potassium thiocyanate, sodium salicylate, and sodium benzoate. The systems are defined, for example, as follows: 7.2 mg. of albumin, dissolved in enough 2.15 N KCNS solution so that the KCNS content was 1.06 grams; the same amount of albumin was dissolved in enough normal sodium salicylate solution so that the sodium salicylate content was 0.32 gram. In order to obtain a clear solution of the coagulated serum albumin these concentrations (in addition to several other concentrations which the author tabulates) had to be rigidly adhered to; greater or lesser amounts would not accomplish the results.

After dialysis of these systems containing peptized albumin, the albumin was found to be again coagulable by heat. It was found that the same salts which peptize the coagulated albumin also prevent its coagulation, much less salt being necessary for the latter than for the former. It is a noteworthy fact that Wilhelm found that both the total quantity and the concentration of peptizing agent with respect to the albumin must be fixed, as is shown from the data above.

From the results obtained, it was concluded that the peptization of the coagulated protein is influenced by two distinct processes. There is first an imbibition of water by the protein; the swollen protein then adsorbs ions from the solution becoming peptized thereby.

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[1] Biochem. Z., **180**, 231 (1927).

[2] Kolloid-Z., **42**, 217 (1929).

The results of Wilhelm controvert the conclusion to which Pauli[1] came concerning the two processes, denaturation and coagulation.

Denatured hemoglobin was repeptized by Anson and Mirsky.[2] Horse hemoglobin was used in this work. Either sodium hyposulphite or potassium cyanide was found to be apparently indispensable to the repeptization of the denatured protein. The system was extracted with toluene during the process. Carbonyl hemoglobin was finally crystallized from repeptized systems which were denatured by heat, acid, and urea. The reversed protein was shown to be identical with the original: by crystallizing the carbonyl derivative, by its restored heat coagulability, and by the fact that it denatured again with acids and alkali.

The conclusion is reached that the coagulation of proteins, in general, is a reversible chemical change which is very obscure.

In another paper Anson and Mirsky[3] discuss denaturation at greater length. They state that it has not yet been proved that the various forms of denaturation are due to the same changes in the protein, for concentrated solutions of urea denature proteins but keep the denatured proteins in solution. When the urea is dialyzed out, the protein precipitates completely.

Anson and Mirsky say that the denaturation of hemoglobin is exactly the same process as the denaturation of albumin. They also say that KI, KCNS, and sodium salicylate probably denature proteins in general, when the protein solution is buffered at $[H^+] = 1 \times 10^{-4.7}$, or near the isoelectric point.

Apparently urea can denature egg albumin, and likewise dissolve the denatured albumin. Egg albumin was allowed to stand in a concentrated urea solution for a day. A few drops of this solution were added to 15 cc of water which was buffered at $[H^+] = 1 \times 10^{-4.2}$. This caused a heavy precipitation. Upon dissolving some urea crystals in the water, the protein redissolved.

In these two papers there is no mention of peptization, the view-point being strictly one of chemical reaction.

The problem to repeptize heat-coagulated egg albumin not having been solved, the present work was undertaken with two purposes in view, i.e., to accomplish this repeptization, and to endeavor to show that so-called denaturation is a colloidal phenomenon and not due to a chemical reaction. For the purpose of this investigation the principles of colloid chemistry will be adhered to as rigidly as the subject will permit, and "the dogma that albumin is an amphoteric electrolyte" will be discarded. It has been shown that it is possible to repeptize serum albumin gels by the use of a variety of reagents and to obtain solutions which are identical with the original. Considered as a problem in colloid chemistry, there is no good reason why this should not be so. This theme will be dealt with more completely further on.

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[1] Hofmeister's Beiträge, **9**, 415 (1908).

[2] J. Gen. Physiol., **13**, II, 133 (1929).

[3] J. Gen. Physiol., **13**, II, 121 (1929).

Experimental Study

In order to observe experimentally the manner in which heat-flocculated egg albumin and egg white behave, from the colloidal standpoint, some rough qualitative experiments were undertaken first.

A portion of the white of a hard-boiled egg was ground in a mortar to a fine powder with solid potassium iodide and cane sugar. Distilled water was added to the mixture. A cloudy sol formed which cleared up somewhat upon the addition of more sugar. Upon performing this experiment several times it became apparent that the amount of peptization depended, as one would expect, to a large extent upon the degree of fineness to which the system was reduced upon grinding.

The selective wetting of heat-denatured, globulin-free albumin by several liquids was next determined. Glycerol and water both wet albumin. When dried and finely ground albumin is put in contact with water the particles show a tendency to form lumps, to agglomerate. With glycerol, however, there is apparently little or no agglomeration. Small samples of albumin were put in contact with chloroform, acetone, and benzene. Upon adding glycerol to each of the systems, the albumin immediately passed into the glycerol layer. Thus, glycerol wets egg albumin preferentially to these liquids. In view of this, the heat-coagulated albumin must be considered as still being hydrophylic, although Bechhold[1] states that heat coagulation changes natural proteins, which are hydrophilic, so that they become hydrophobic. What actually happens is that they lose most of their water sheath.

Cold coagulation (Kältefällung) of albumin is said to be irreversible. However, it was found that freezing the white of an egg and then lowering the temperature below minus 10° did not visibly affect the physical condition of the sol when it again comes to room temperature. It will later be shown that this is exactly the behavior that would be expected of such a sol.

Following the lead of Spiegel-Adolf,[2] we tried to repeptize heat-coagulated egg albumin with sodium hydroxide solution. The globulins were precipitated out of an absolutely fresh egg-white sol by the approved method. The globulin-free albumin was coagulated by heating it in boiling water for fifteen minutes. The lumps of coagulated albumin were filtered off and washed several times with boiling distilled water. Five systems were prepared using this sample; 16 grams of the wet sample were put into a flask with 100 cc. of distilled water and 0.7 gram of sodium hydroxide; 10 grams of the wet sample were put with the same amounts of sodium hydroxide and water; five grams of the wet sample were put with one-half the amount of sodium hydroxide and the same amount of water; 0.5 gram of the albumin was put with 5% of the amount of sodium hydroxide in the same amount of water, and finally; 16 grams of the wet albumin were put with 2.1 grams of sodium hydroxide and 100 cc. of water. All of the systems, except the last, were agitated on a shaking machine for 3 days. The last system became clear, with all of the albumin apparently peptized, in the course of 17 hours. The others failed to peptize to any marked extent. The system containing the peptized albumin was dialyzed against running distilled water for about 30 hours. The sol was then found to have the following physical and chemical characteristics. It was neutral to litmus, alkaline to methyl orange, and slightly alkaline to phenolphthalein. It was odorless, and absolutely clear and colorless. The xanthoproteic and biuret reactions were positive. It coagulated with heat only upon making it acid to phenolphthalein but not adding enough acid to make it acid to methyl orange. Ammonium sulphate was used to change the alkalinity of the sol. The addition of glacial acetic acid caused a heavy precipitation. In the presence of alcohol and sodium chloride, the sol did not coagulate when heated to above 78°. It required less than half-saturation with ammonium sulphate to precipitate large quantities of the colloid.

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[1] "Die Kolloide in Biologie und Medizin," 164 (1929).

[2] Alexander: "Colloid Chemistry," **2**, 309 ff. (1928).

Because of the slight dissimilarities between this sol and uncoagulated albumin we cannot at the present time conclude that the albumin did not suffer some slight hydrolytic cleavage during repeptization.

The statement[1] has been made that ether denatures egg albumin. Upon investigating this phenomenon quite the reverse was found to be true, under certain conditions. Fresh egg white was diluted with distilled water to form a 10% sol. Globulins, of course, precipitated; they were filtered off as completely as possible. The sol was extracted twice with ether. Quite a stable emulsion persisted at the ether-sol interface. The ether was gently boiled out of the extracted sol. The addition of alcohol to this sol produced no coagulation whatever. Alcohol did precipitate it when enough was added so that the dispersion medium was more than a 50% solution of alcohol. The effect of heat was determined by immersing the sol in a test tube in boiling water for 15 to 20 minutes. The sol remained clear; absolutely no coagulation took place.

This was too good, so that the obvious explanation that most of the albumin had concentrated at the interface was tested. The xanthoproteic reaction was tried on the sol. The addition of nitric acid resulted in heavy coagulation. To check this test, glacial acetic acid was added to the sol; again a large amount of precipitate came down. The whole experiment was repeated several times with the same results. A portion of the sol which was not extracted with ether coagulated normally upon immersing the test tube containing it in boiling water.

This method of preventing coagulation was tried on a 50% egg white sol (50 cc. egg white diluted with 50 cc. of distilled water). The result was the formation, upon heating, of a slight amount of coagulum, which was manifest by the appearance of a heavy cloud in the sol. A far larger amount of precipitation occurred upon the addition of either acetic acid or nitric acid.

A striking difference in properties between the native egg-white coagulum and that produced when an ether-extracted sol was coagulated by heat in the presence of a little acetic acid is observable. The untreated sol coagulates into lumps, or into one solid mass, depending upon the conditions. The ether-treated sol, when coagulated by heat in the presence of a little acetic acid comes down in the form of strings. The dense precipitate is apparently more highly hydrated than the string-like precipitate; its probable classification is as a curdy[1] precipitate. The other precipitate would then be classified as a flocculent precipitate, or as will be shown in a later paper more probably as a jelly. In this case there is apparently a rather sharp line between flocculent and curdy precipitates. The ether under this classification must stand trial for the removal of something which makes the water sheath of the colloidal albumin particles less strongly adsorbed; or else the ether itself is held by the albumin thus making its water sheath less strongly adsorbed. Coagulation, under this last hypothesis, must start before the ether is removed from the albumin particles by the heat.

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[1] Lepeschkin: Kolloid-Z., 32, 100 (1923); Hammarsten: "A Textbook of Physiological Chemistry," 107 (1914).

It has been shown that ether can be used to prevent heat coagulation. If heat coagulation were due to a chemical reaction, it is difficult to see just how the ether extraction of the sol would prevent it. How ether could react with an amino group, an imino group, a carbonyl group, a sulphhydryl group, a carboxyl, or phosphorus group is not at all obvious. Further, how it could, in this case, form a heat-stable addition product, cause hydrolysis, or open an internal anhydride ring is equally hard to see. Also, the ether was free from peroxide by actual test; so that that could not have been responsible for the condition which was brought about. Therefore, the burden of the proof is upon him who claims that this phenomenon is due to a chemical reaction.

The ether removes something from the albumin sol. There was a distinctly measurable amount of residue upon evaporation of the ether which was used for the extraction. The solid material is apparently soluble in ether and peptizes in water; for the solution remained clear until most of the ether was evaporated off. Then, when the water content became greater than the ether content, the system became cloudy. The sol so formed was diluted with water and an electrophoresis experiment performed upon it. The sol was discharged from both electrodes with a greater amount of discharge from the anode than from the cathode. This must mean that there are two substances present, one charged negatively and the other positively, the one charged negatively predominating.

The concentrated extract apparently coagulates a 10% albumin sol, for it became decidedly more turbid upon addition of the extract.

It is interesting to note the results obtained by an electrophoretic study of three lecithin sols. The lecithin was prepared from egg yolk.[2] The first sol was prepared by shaking lecithin with water and drawing the air out of it by means of a vacuum pump. As was expected,[3] the suspended particles travelled toward the anode, showing that they were negatively charged. The second sol was prepared by adding an alcoholic solution of lecithin to about a 20% alcohol-water solution. The suspended particles were apparently discharged at both the anode and the cathode, with the larger amount of discharge at the anode. The third sol was the same as the first; only it was heated to about 90° before the electrophoresis was started. It behaved, not like the first sol, but like the second.

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[1] Bancroft: "Applied Colloid Chemistry," 193 (1926).

[2] Webster and Koch: "Laboratory Manual of Physiological Chemistry," 1 (1903).

[3] Kakiuchi: J. Biochem. (Japan), 1, 165 (1922).

An analysis of egg white[1] shows that the amount of fat, including lecithin, present is 0.25%. From these facts it is obvious that the thing partly responsible for heat coagulation may be a fatty material associated with lecithin, but having under certain conditions an opposite charge. The plus charge that this substance has would then be partly responsible for the flocculation of the protein from suspension upon heating.

When one allows undiluted egg white to stand with enough ether for an appreciable time, it does, as has been maintained, coagulate. This is quite obviously due to the removal of water, not from the albumin molecule, but from the sheath of water surrounding the individual suspended albumin particles.

The white of an egg was diluted 50% with distilled water and coagulated by immersion in boiling water. Part of the substance prepared in this manner was extracted for eight hours with peroxide-free ether, by merely allowing the ether to stand in contact with the egg white, and changing the ether frequently. The ether was drained off of the sample and a portion of it was put in 125 cc. of distilled water containing a fairly large amount of ammonium thiocyanate. The system was agitated on a shaking machine. In about 24 hours the appearance of the sol indicated that considerable peptization had resulted. The ether extraction of a portion of the coagulated egg white was continued until the ether, as a result of many changes, dried the egg white to a hard, transparent mass. Three experiments were performed upon this material. A small amount of it was put into each of the following: 15 cc. of water containing about two grams of ammonium thiocyanate, 15 cc of water containing about two cc. of ammonium phosphate solution (prepared by neutralizing syrupy phosphoric acid with ammonium hydroxide and adding enough base to produce a faint ammoniacal odor). The three test tubes were shaken on a machine for three and a half days. At the end of this time it could be seen that in the case of the latter two experiments peptization occurred, whereas, with the pure water there was no peptization. The three systems were heated to the boiling point. The system containing only albumin and distilled water became quite cloudy during this process; the other two did not change markedly.

Another portion of the coagulated egg white described in the paragraph above was extracted with peroxide-free ether for three days in a Soxhlet extractor. A portion of the albumin thus obtained was placed in water and the system boiled for about ten minutes. A cloudy sol formed. It was further broken up by stirring by means of a high-speed soda mixer. This was followed by shaking for 12 hours on a shaking machine. The result was the formation of a very cloudy albumin sol. Heating separate portions of this sol with ammonium thiocyanate, potassium iodide, and starch revealed the fact that the sol became less cloudy (accompanied by no precipitation) in the case of the first compound but did not change in appearance with the other two. The sol containing ammonium thiocyanate was acid to litmus. Sodium bicarbonate was added to neutralize it. This resulted in the liberation of ammonia and the sol at the same time became quite clear, indicating more or less complete peptization.

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[1] Hutchinson: "Foods and Dietetics," 148 (1900).

When the coagulated and extracted protein was boiled with water in the presence of ammonium thiocyanate there was no visible amount of peptization. The difference between this case and the case above, where the peptizing agent was added after the boiling seems to be concerned with the swelling of the albumin particles. When the electrolyte was present during boiling the amount of swelling appeared to be distinctly less than when it was added after the system was boiled and had cooled to room temperature.

The effect of various reagents which could reasonably be presumed to exert a peptizing action upon coagulated egg white was next studied. The sample was prepared by diluting egg white with an equal volume of water and heating the sol so formed for 15 minutes in boiling water. The coagulum was extracted for 72 consecutive hours with ether. When the extraction was completed the coagulum was found to be very dry. Upon placing a portion of it in boiling water peptization occurred. A large volume of this sol was then prepared. The effect of peptizing agents was tried on separate portions of the sol. Potassium thiocyanate in an amount such that it was very concentrated in respect to the electrolyte was added to 15 cc. of the sol. After shaking by hand for a few minutes and allowing to stand for a day the sol was quite cloudy. The addition of a little glacial acetic acid caused considerable precipitation. This shows us that there was a significant amount of coagulated albumin peptized by the water and the electrolyte. The experiment was repeated using potassium iodide. This time the glacial acetic acid produced a very large amount of coagulation when added to the sol. When the experiment was tried using cane sugar instead of an electrolyte peptization takes place. The sol so produced does not coagulate when glacial acetic acid is added. Nitric acid does, however, cause coagulation. It has been found[1] that both sulphur dioxide and formaldehyde prevent the heat coagulation of albumin sols. It was also found that this property is probably not dependent upon reduction because other reducing agents were without effect. One-half cubic centimeter of formaldehyde was added to 10 cc. of the sol and the system was agitated for a short time. In two days the sol was tested for peptized protein by adding acetic acid. There was no precipitation. However, nitric acid caused a noticeable amount of coagulation. Gortner[2] states that formaldehyde combines with the proteins, whereas there is apparently no evidence, in the case of egg white, that the action is anything other than a peptization.

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[1] Munaretto: Arch. farm. sper., **14**, 460.

[2] "Outlines of Biochemistry," 404 (1929).

Because of the utility of a good chemical test for albumin at this stage of the work the sodium nitroprusside ($Na_2Fe(CN)_5NO.5H_2O$) test[1] was examined critically. The test is stated to be for the presence of an SH group. It is performed by adding to one to two cubic centimeters of the substance to be tested an excess of finely powdered ammonium sulphate. This is followed by two to four drops of a freshly prepared 5% sodium nitroprusside solution. The system is made alkaline by the addition of a few drops of ammonium hydroxide. A magenta color indicates the presence of denatured protein. The author states that crystallized egg albumin gives no reaction when this test is applied but that albumin coagulated by heat or acetic acid gives the test immediately. Egg white evaporated on an extensive surface showed only a doubtful nitroprusside reaction, when tried by Harriss.

When dried egg white was suspended in water it was found to give a distinctly positive reaction upon performing this test. The white of an egg was diluted to one half with distilled water and coagulated by heating in boiling water for 14 minutes. The gel was cooled and the nitroprusside reaction tried on a portion of it. No reaction was noticeable. These experiments were repeated with the same results as before. The experiments were then repeated twice again, allowing more time for the reaction to take place and varying the amount of sodium nitroprusside solution used. The results were no different this time. Finally the test was carried out on a sodium thiosulfate solution which was acidified with a little acetic acid. A magenta-colored ring formed where the ammonium hydroxide came in contact with the body of the liquid. From this it would appear that colloidal sulphur also gives the nitroprusside test for denaturation.

These experiments indicate that this test is not to be regarded as reliable enough for our use in studying heat coagulation, for it may fail to work when it should, and it may be positive when it should be negative.

The effect of dextrose upon heat coagulation was studied briefly. A 15% egg white sol was not prevented from coagulating by the addition of 0.25 gm of dextrose to 10 cubic centimeters of the sol. However, when the sol was saturated with respect to dextrose heating in boiling water caused no coagulation. Considering this from the colloidal viewpoint it offers an explanation for the peptizing action of cane sugar upon coagulated albumin. We shall see later just how this ties in.

Having repeptized coagulated egg white, and, further, having prevented the coagulation of egg white sols it now only remains to be shown that the repeptized sols are chemically identical with the original sol. For this purpose the immuno-biological reaction known as the precipitin reaction was chosen.[2]

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[1] Harriss: Proc. Roy. Soc., 94B, 426 (1923).

[2] Our thanks are gratefully extended to Professor W. A. Hagan, Head of the Department of Veterinary Bacteriology of the New York State Veterinary College at Cornell University for his supervision of and help with this part of the work.

The protein precipitins are highly specific. They show their characteristic reaction only with the proteins which were used in preparing them.[1] Investigating the effect of chemical and physico-chemical changes of the protein molecule upon its antigenic behavior, Obermayer and Pick[2] state that both types of change prevent its visible reaction with native immune serum. Pick[3] came to the conclusion that agencies which effect, even in the slightest degree, the properties of the proteins lessen or completely prevent their antigenic behavior.

Anson and Mirsky[4] found that upon reversing denatured hemoglobin the specificity, which was lost in the denatured protein, is restored in the regenerated product.

Jordan[5] says: "Particular groups within the protein molecule—the amino-acids—are probably responsible for the specificity of anaphylaxis and other antigen-antibody reactions. Both chemical composition and isomeric arrangement doubtless play a part in the close correspondence that exists between antigen and antibody."

The precipitin reaction, therefore, is an extremely sensitive test for establishing the chemical identity of coagulated, repeptized albumin with native albumin.

Fresh egg white was diluted with distilled water to form a 15% egg white sol. The system was agitated for less than ten seconds under a high speed soda mixer to homogenize it. Globulins precipitated out. They were removed by passing the sol through coarse filter paper three times. It was allowed to stand for two days, during which time incipient precipitation occurred, and then it was filtered three more times using ashless filter paper. The sol so prepared was passed through a sterilized Berkefeld filter.

Five cubic centimeters of the sterile sol was injected intravenously into each of two rabbits. One week later ten cubic centimeters of the sol, which had been kept at 4°, was injected into each rabbit. After a lapse of two weeks ten cubic centimeters of a freshly prepared sol was again injected into each rabbit. Finally, five days later the rabbits were injected with the third ten cubic centimeter dose, this time subcutaneously. Ten days were allowed for the serum to build up its titer. The rabbits were then bled, the blood centrifuged, and the serum recovered. This serum was used for the precipitin reaction.

Two methods for repeptizing heat-coagulated egg white were used in preparing the antigen for the precipitin reaction. The white of an egg was diluted with distilled water to make a 50% homogeneous egg white sol. The system was heated in boiling water for 15 minutes to coagulate the protein. It was brought to room temperature and 85 cc. of distilled water added. Chemically pure urea was added to the system until it was practically saturated. The large test tube containing the system was shaken moderately for 24 hours with the addition of small amounts of urea from time to time. The sol so formed was cloudy. A portion of it was dialyzed against running distilled water using a small parchment dialyzing thimble. The size of the dialysate container and the rate of flow of the water were so arranged that there was the equivalent of a complete change of the water every 20 to 30 minutes. The sol was dialyzed for three days; at the end of that time the dialysate showed no residue upon evaporation at room temperature under a vacuum. The sol so produced was cloudy, but contained invisible particles as proved by the precipitation with acetic acid. The other sample was prepared from a 50% egg white sol as above. Ether, to the extent of three times the volume of the coagulum, was poured on top of the cooled coagulum. The system was allowed to stand for a couple of hours in contact with the ether. The ether was poured off and another portion added; this was also allowed to stand for two hours. Immediately upon pouring off this second portion of the ether, part of the coagulum was put into distilled water and heated on a boiling water bath. This treatment drove off the ether and at the same time mechanically disintegrated the albumin particles; the expanding ether probably burst the particles. The albumin then began to imbibe water and further reduce in size. The water sheath is thus, at least in part, restored to the particles, causing them to stay suspended. Potassium thiocyanate was then added to the sol until it was almost saturated. This was accompanied by a distinctly visible decrease in the cloudiness of the sol. At the same time there was no precipitation of the colloid particles. The clearing up was due, therefore, to further peptization of the albumin, by the thiocyanate ion. This sol was dialyzed in the same manner as the one previously described. Again there was a significant amount of albumin in suspension as proved by its precipitation upon the addition of acetic acid. At the end of three days neither the sol nor the dialysate contained the thiocyanate ion as proved by the absence of the red color upon the addition of ferric chloride solution. Both of the sols just described formed an absolutely clear colloid suspension when diluted one to ten with physiological salt solution.

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[1] Spiegel-Adolf: Alexander's "Colloid Chemistry," 2, 311 (1928).

[2] Wien. Klin. Rundschr., 1902, No. 15; Wien. Klin. Wochenschr., 1903, 659; 1906, No. 12.

[3] Beitr. Chem. Physiol. Path., 1, 445 (1902.)

[4] J. Gen. Physiol., 9, 169 (1925).

[5] "A Textbook of General Bacteriology" 193 (1929).

The precipitin reaction was studied by adding the undiluted serum to portions of the two sols which were diluted with physiological salt solution. Approximately 0.2 cc. of the rabbit serum was layered against an equal amount of the antigen in its various dilutions. The following tabulation shows the results that were obtained.

TABLE I

Dilution of Antigen	Reaction of $CO(NH_2)_2$ Repeptized sol	Reaction of KCNS Repeptized sol	Reaction of untreated 15% egg white sol	0.85% NaCl Solution
1;10	+ +	+ + +	+ + +	o
1;100	+	+ +	+ +	
1;1000	o	+	+	

From the data obtained from this reaction it seems quite obvious that urea and potassium thiocyanate both repeptize heat-coagulated egg albumin. Furthermore, it appears certain from these tests that the heat-coagulated and repeptized albumin is chemically no different from the original material.

That the precipitin reaction is extremely specific is also shown by the results of a test performed on egg albumin which was coagulated by alcohol and repeptized by concentrated potassium thiocyanate and six drops of N/20 sodium hydroxide per 40 cc of the sol. Although it was evident that there was repeptization, the dialyzed sol showed no precipitin reaction. This, in addition to what others have found, apparently established beyond a doubt that the test as used here, for this specific purpose, using as antigen and precipitin those things which were used, and only those things, is extremely highly specific. The case of alcohol coagulation will be considered later on.

Although the whole white of an egg was used in this work, there can be no question about whether the globulin was responsible for the precipitation or not. The simple answer to that is that there was no globulin present. Globulins are insoluble[1] or more correctly, form such unstable sols in pure water that they will, as we have seen, precipitate out of an egg white sol upon merely diluting[2] it with distilled water. Ostwald finds that a 10% egg white sol in distilled water contains practically no globulin.

Since native egg white sols that do not contain too large an amount of the disperse phase stay in suspension at the isoelectric point, the claim is made that to prove the identity of the repeptized protein with the native material, it too should not precipitate when brought slowly to the isoelectric point. Quite obviously the native albumin, which stays up at the isoelectric point, is the abnormal case; whereas, the repeptized material which comes down at the isoelectric point acts as it should.

Repeptization of heat-coagulated egg-white sols, using ether to produce mechanical disintegration, gives us a sol which does not precipitate completely when it is brought slowly to the isoelectric point. When the experiment is not carried out correctly, however, the protein precipitates quantitatively upon bringing the sol to the isoelectric point. In other words, the system protein-ether should undergo a sudden and large temperature change when it is immersed in hot water.

Thus, we have advanced further proof that the coagulation of an egg white sol is a reversible physical change, if one is willing to believe that similarity of behavior at the isoelectric point proves anything about chemical constitution.

Many heat-coagulated egg-white sols that are repeptized do not stay up when they are brought slowly to the isoelectric point. The apparent reason for this is that the initial heating destroys the action of some protecting colloid that is present in the original system. This principle is illustrated by the following experiment. When enough Congo Red sol is added to a repeptized albumin sol that would itself precipitate at the isoelectric point, the albumin does not all come down when the system is brought slowly to a pH of 4.8, the isoelectric point of egg albumin.

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[1] Ostwald: "Practical Colloid Chemistry," 159 (1924); Sumner: "Bio logical Chemistry,' 86 (1929); Lloyd: "Chemistry of the Proteins," 44 (1926).

[2] Ostwald: "Practical Colloid Chemistry," 157 (1924).

These experiments prove, therefore, that heat coagulation is strictly a reversible change. How the reversible change can be chemical rather than physical is not obvious. For instance, how potassium thiocyanate, urea, potassium iodide, sodium hydroxide, cane sugar, formaldehyde and ammonium phosphate, in the case of egg albumin, potassium thiocyanate, sodium salicylate, sodium hydroxide, and sodium benzoate, in the case of serum albumin, could each cause the reversal of the same chemical change (were heat denaturation a chemical change) is not at all apparent. These compounds possess no characteristic which is common to all of them; some are alkaline in water solution; while others are neutral; some are electrolytes while others are not; some are reducing agents and others are not. Yet, this divers array of compounds all cause albumin of one kind or another to assume its original form after heat coagulation.

Anson and Mirsky[1] have said that the denaturation of proteins is a truly reversible process, but it is ordinarily masked by the flocculation of the denatured protein. Had the authors inserted the word colloidal, their statement would have completely covered the case as it apparently is.

So-called denaturation has been shown to be a colloidal phenomenon and therefore responsible to the rules of colloid chemistry. The actual mechanism of heat coagulation as well as other types of coagulation of this protein, being somewhat more involved than the mechanism of peptization of the coagulated protein, will be discussed at length in another paper.

If, then, one is willing not to be mystified by the word protein, the word "denaturation" should go by the boards; for we already have in the nomenclature of colloid chemistry terms which describe the process accurately.

The conclusions to be drawn from this paper are:

1.—"Denaturation" has been assumed to be a chemical change.

2.—A satisfactory theory has not been offered for this change.

3.—Other workers have retarded, prevented, and reversed "denaturation."

4.—The problem has not, up to this time, been considered from a strictly colloid-chemical view-point.

5.—Regarding egg albumin as a hydrophilic colloid, the problem to peptize heat-coagulated egg-white sols has been undertaken and solved.

6.—Potassium iodide, potassium thiocyanate, urea, ammonium thiocyanate and sodium bicarbonate, formaldehyde, and cane sugar all peptize heat-coagulated egg-white sols.

7.—Sodium hydroxide was found to peptize heat-coagulated albumin, although there is some possibility that a slight amount of hydrolysis occurred.

8.—Ether does not denature albumin under ordinary conditions.

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[1] J. Gen. Physiol., 9, 169 (1925).

9.—Egg-white sols were prevented from coagulating by extracting them with ether.

10.—It is difficult to see how ether could prevent any conceivable chemical reaction that might take place upon heat coagulation.

11.—Therefore, ether prevents "denaturation" by some sort of colloidal mechanism.

12.—The ether probably extracts something from the sol, thus giving it heat stability.

13.—The extracted material was studied as a colloid.

14.—It was shown how it can act as a coagulating agent.

15.—The substance acted like crude lecithin from egg yolk.

16.—"Denaturation" by means of ether, which does occur under some circumstances, is due merely to the removal of adsorbed water from the colloid.

17.—Coagulated egg white repeptizes in boiling water, specially when it contains some ether to disintegrate the particles mechanically.

18.—The presence of electrolytes during heating apparently prevents swelling.

19.—The sodium nitroprusside test for "denatured" egg albumin was found to be wanting.

20.—Dextrose prevents heat coagulation when present in large enough amounts.

21.—Immuno-biological tests for species specificity have shown that coagulated and repeptized egg-white sols are identical with the original, as also have isoelectric point measurements.

22.—A mechanism of peptization has been proposed which initially involves mechanical disintegration of the protein coagulum by hot water, aided in some cases by ether, and followed by further disintegration and peptization by the negative ions of various electrolytes.

23.—The dogma of denaturation has been deleted.

Cornell University.

SWELLING AND HYDRATION OF GELATIN[1]

BY JOHN H. NORTHROP AND M. KUNITZ

The swelling of gelatin when placed in aqueous solutions may be readily separated into three types: 1. Swelling in acid or alkali. 2. Swelling on addition of small amounts of water to dry gelatin. 3. Swelling of dilute gels of isoelectric gelatin in water or in salt solutions.

The swelling in acid or in alkali and the effect of neutral salts on this swelling have been shown by the work of Procter and Wilson,[2] and Loeb[3] to be due to the osmotic pressure of the ions of the electrolyte, in accordance with the Donnan equilibrium. The initial swelling of dry isoelectric gelatin in water—which evidently is not connected with the Donnan equilibrium—has been carefully studied by Katz,[4] who was able to show that the heat effects, volume, pressure, and vapor changes were strictly analogous to those observed in the formation of concentrated solutions of many substances, and that the system as a whole behaved as an ideal concentrated solution. When sufficient water has been added, however, to reduce the gelatin concentration to less than 50 per cent, the heat effects become very small and yet the gelatin may swell, under favorable conditions, until the concentration of gelatin is 5 per cent or less. The third type of swelling has peculiarities which cannot be reconciled with the idea of solution or of hydrate formation and it will be considered here as a distinct type. It is this type of swelling which is discussed in the present paper.

The behavior of gelatin when placed in water has been described by a number of investigators. The more striking peculiarities may be briefly described as follows. In general the swelling increases with the temperature and with the concentration of gelatin. At a concentration of about 10 per cent at 5°C no change in volume occurs, while below 10 per cent the gelatin loses water instead of swelling. A block of gelatin which was brought to a definite concentration by allowing water to evaporate from a dilute gel swells much more than a similar block made by allowing a sol of the same concentration to set. Thin films of gelatin swell to a value which increases only slowly with time while large blocks do not give any indication of a maximum value but continue to swell until dissolved. At higher temperatures there is still less indication of an equilibrium value. If a block of gelatin is allowed to remain in water until it has stopped swelling and then is raised to a higher temperature in air for a short time under such conditions that there is no change in volume, it will swell rapidly when replaced in water at the first temperature.

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[1] The work reported in this paper is a summary of a series of papers on swelling and hydration of gelatin published in J. Gen. Physiol., 1926-1930.

[2] J. Chem. Soc., **109**, 307 (1916).

[3] "Proteins and the Theory of Colloidal Behavior," 2nd Ed (1924).

[4] Kolloidchem. Beihefte, **9**, 1 (1917-18).

Previous Theories of Swelling

A number of theories have been proposed to account for these peculiarities.[5] Hardy assumed that a gel was a solid in contact with its saturated solution. Katz assumed that the gel is a solid solution of water and gelatin, and that the gel is therefore one phase. (The writers agree with this idea for very concentrated gelatin-water systems.) Lloyd suggests that gelatin is made of two components, isoelectric gelatin which is insoluble, and gelatin salts which

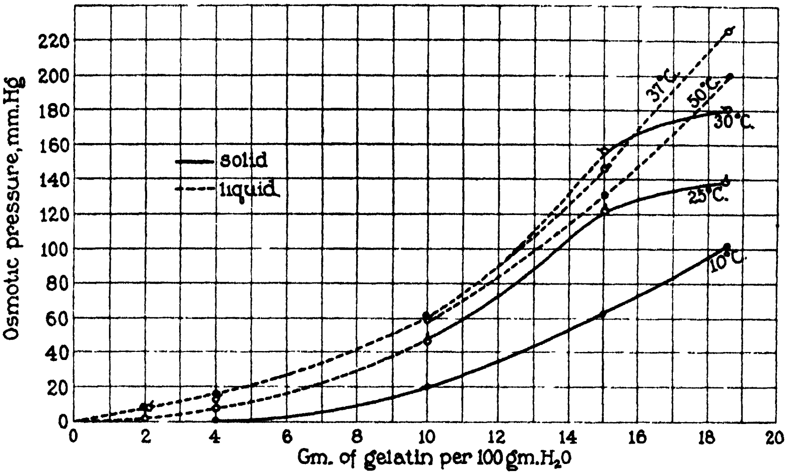

FIG. 1

Concentration and swelling or osmotic pressure of gelatin at different temperatures

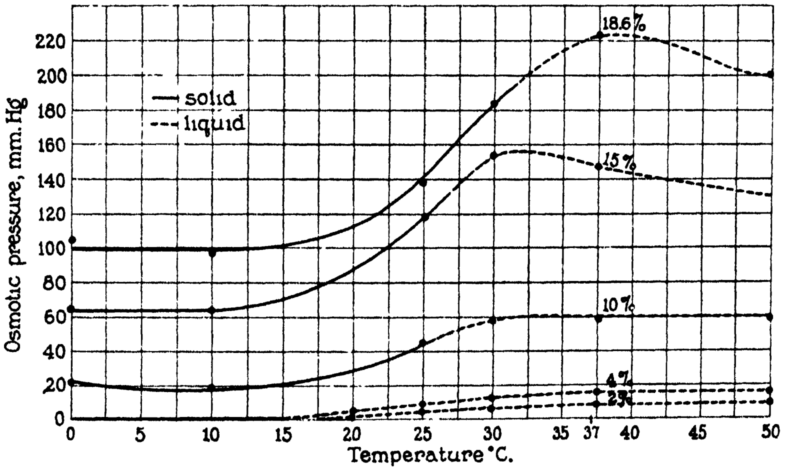

FIG. 2

Osmotic or swelling pressure of various concentrations of gelatin at different temperatures are soluble. Swelling is due to the osmotic pressure of the soluble gelatin salts. A number of other workers have outlined more or less similar theories.

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[5] Cf. Weiser: Bogue's "Theory and Application of Colloidal Behavior," 1, 377 (1924); Bradford: Alexander's "Colloid Chemistry," 1, 751; Lloyd: 767 (1925); Freundlich: "Kapillarchemie" (1923).

It would evidently be a great help in attempting to determine the nature of gels if the number of phases present could be determined. This could be done directly by an analytical phase rule study except for the fact that the (assumed) liquid phase is held in the meshes of the solid and cannot be separated from it, so that the concentration of gelatin in the liquid phase cannot be determined. Since the osmotic pressure is proportional to the concentration, the concentration could be determined indirectly by means of the osmotic pressure; and osmotic pressure-temperature or osmotic pressure-concentration curves could be used in the phase rule diagram. The osmotic or swelling pressure of gels, however, cannot be determined in the same way as the osmotic pressure of liquids owing to the mechanical resistance of the gel. It was found possible to obtain values for the swelling pressure of dilute gels by placing the gel outside a rigid membrane and measuring the pressure required to prevent the entrance of water. The swelling or osmotic pressure curves for different concentrations of gelatin at different temperatures were measured in this way.[6] The results of these measurements are shown in Figs. 1 and 2.[7] The osmotic pressure increases with both temperature and concentration but there are no breaks in the curves at the point where the system becomes solid. If the phase rule be applied to these results it follows that no new phase appears when gelatin-water systems change from liquid to solid either by lowering the temperature or increasing the concentration of gelatin. The number of phases present in the system gelatin-water is therefore the same in either the liquid or solid form. It also follows that there is always present one more component than there are phases, since the system still has one degree of freedom, although the temperature and pressure are fixed. Therefore, if the phase rule is applied in its usual form, it must be assumed either (1) that there are two components, water and gelatin, and that the solid and liquid forms are the same phase, or (2) that there are three (or more) components and two (or more) phases. If n phases are assumed there must be n + 1 components.

The first possibility would agree with the idea that the system is a solution which may be either liquid or solid depending on the composition. It is not possible to assume that it consists of a solid phase of one component in equilibrium with its saturated solution since in the presence of the solid the system would be fixed if the temperature and pressure were fixed.

It is probable that the concentrated gels studied by Katz are solid solutions of water and gelatin, as Katz concluded. It is very difficult, however, to account for the properties of the more dilute gelatin sols or gels on this basis owing to the peculiar hysteresis effects noticed in swelling experiments and the changes in viscosity with time, temperature and pH. The hysteresis effects, on the other hand, are exactly what would be expected of an elastic solid (or of a suspension). The facts that the swelling of gels at low temperatures reaches an equilibrium value and that gels of less than 10 per cent concentration lose water instead of imbibing water, also contradict the assumption of a solution. In general therefore the assumption that dilute gelatin-water systems consist of two phases seems in much better agreement with the facts. It follows then from the pressure measurements summarized above that the system must consist of (at least) three components and since water is certainly one, gelatin must contain the other two. It was assumed therefore as a working hypothesis that the system gelatin-water, whether in the sol or gel state (at a concentration of less than 40 per cent gelatin) consists of (at least) two phases, one solid and one liquid, and (at least) three components, water, "soluble" gelatin, and "insoluble" gelatin.

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[6] Northrop and Kunitz: J. Gen. Physiol., **10**, 161 (1927).

[7] Since gels below 10 per cent lose water the swelling-pressure curve must cross the concentration axis at about 10 per cent gelatin content and then becomes negative. This could not be determined in the form of apparatus used since negative pressures would not be recorded.

There are two possible systems which agree with the osmotic pressure measurements: 1. The solid phase is a solid solution of "soluble" and "insoluble" fractions of gelatin and water. The liquid phase is an aqueous solution of the "soluble" and "insoluble" fractions of gelatin. 2. The solid phase is the "insoluble" fraction alone and the liquid phase is a solution of the "soluble" and "insoluble" fractions. In either case the solid phase exists in the sol state as finely divided particles—*i.e.* micellae.

The facts observed in connection with the viscosity of sols and syneresis of gels, however, necessitate the assumption of structure in the particles (micellae) of solid present, since, in order to account for these results it is necessary to assume that the micellae contain liquid phase and that the concentration of gelatin in this "internal" liquid phase is higher than that in the bulk of the liquid phase surrounding the micellae, with the result that the micellae take up water, or swell.

It is difficult to derive this condition from the assumption that the solid phase is a solid solution and it is therefore necessary to conclude that the micellae form a separate system, consisting of an elastic membrane of insoluble gelatin, in equilibrium with the "external" liquid phase and containing an internal liquid phase which is a solution of one or more partly "soluble" components. The walls of the micellae are impermeable to these components. In the sol state therefore gelatin consists of a suspension of micellae in a solution of the "soluble" and "insoluble" components. These micellae are in equilibrium with the surrounding solution, the difference between the osmotic pressure inside and outside of the micellae being balanced by the elastic resistance of the walls. They are therefore capable of swelling or contracting as Loeb assumed. As the total concentration of the sol increases the osmotic pressure of the external liquid-phase increases, while that of the internal liquid remains the same so that the micellae swell less in concentrated sols. This accounts for the effect of concentration on the viscosity and also, as will be shown later, for syneresis of dilute gels.

As the sol is cooled or as more gelatin is added, the amount of the "insoluble" fraction present as solid increases, and the micellae increase in size and possibly in number. When they occupy a large enough proportion of the total volume the "insoluble" fraction becomes connected to form an elastic network and the sol becomes a gel. The liquid phase surrounding the micellae still contains the "soluble" component in solution and therefore has an osmotic pressure. When a block of gel is placed in water this osmotic pressure causes water to enter and the block swells. As swelling continues the osmotic pressure becomes less owing to dilution, and at the same time an elastic stress appears in the block owing to the stretching of the elastic network. When this elastic stress is equal to the osmotic pressure the system is in equilibrium and swelling stops. Under certain conditions the osmotic pressure of the solution in the micellae is decreased on cooling so that water is forced out of them by the elastic contraction of the walls of the micellae. Under these conditions the block as a whole may lose water.

Any conditions therefore such as higher temperature or strong salt solutions which increase the solubility of gelatin will increase the swelling. The elastic stress of the block shows fatigue as do all elastic bodies and this fatigue accounts for the hysteresis effects and for the difference in the swelling of large and small blocks.

The picture of gel formation and the mechanism of swelling outlined above is similar to that proposed by Duclaux[8] for the swelling of rubber and published during the course of the present work; a somewhat similar mechanism had also been proposed previously by Lloyd.

This mechanism has been found adequate to account qualitatively for all the properties of gelatin of which the writers are aware and quantitatively for a large number. It has predicted several properties which had not been suspected.

Application of the Hypotheses to the Properties of Gelatin

Hydration of Isoelectric Gelatin as determined from Osmotic Pressure and Viscosity Measurements.[9]

Figures 3 and 4 give the curves for osmotic pressure and viscosity of sols of various concentrations of isoelectric gelatin at 35°C. On the same figures are drawn, for comparison, curves for osmotic pressure and viscosity of electrolyte-free isoelectric egg albumin measured at 20°C. The osmotic pressure-curve for egg albumin is a straight line, while in the case of gelatin the curve rises rapidly with increase in concentration of gelatin. The same difference is shown by the viscosity curves. The viscosity of gelatin even in low concentrations is much higher at 35°C than the viscosity of egg albumin at the corresponding concentrations and increases enormously with increase in concentration. This difference in the behavior of egg albumin and gelatin with respect both to osmotic pressure and viscosity is explainable by the difference in their degrees of hydration.[10] Egg albumin is hydrated very little, while gelatin is highly hydrated even at 35°C. The high degree of hydration of gelatin is due to the swelling of the micellae which, in turn, is caused by the difference in the concentrations of gelatin in the internal and external liquid phases.

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[8] Bull., 33, 36 (1923).

[9] Kunitz: J. Gen. Physiol., 10, 811 (1927).

[10] Kunitz: J. Gen. Physiol., 9, 715 (1926).

It is possible to determine approximately the degree of hydration of gelatin independently from both osmotic pressure and viscosity measurements.

Osmotic Pressure and Hydration of Gelatin.—The osmotic pressure of a dilute molal solution of a hydrated substance may be expressed[10] as

$$P = K \frac{C}{1 - \varphi}$$

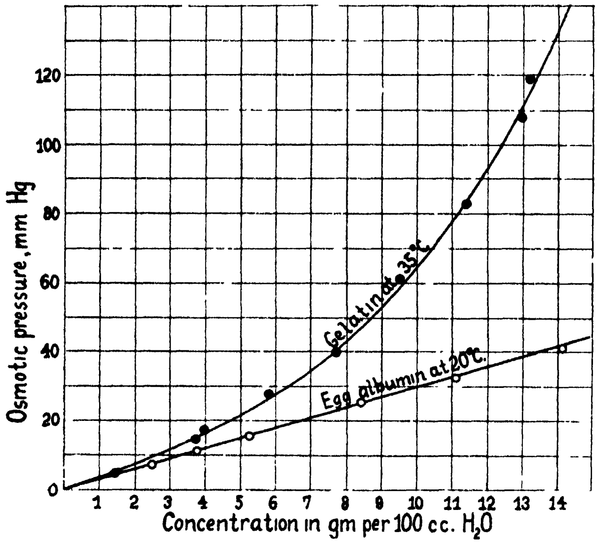

Fig 3

Osmotic pressure curves of isoelectric gelatin at 35°C and of isoelectric egg albumin at 20°C.

where $K = RT/M$ (M = mole weight of solute)

C = gm. of solute per cc of solution

φ = volume of C gm of the hydrated solute

which means that the osmotic pressure is proportional to the concentration, expressed as moles per cc. of free solvent.

The value of φ can be calculated from the osmotic pressure measurement if K is known.

From the relation

$$K = P/C\,(1 - \varphi)$$

it follows that as C approaches zero, $\varphi \doteq 0$ and $K \doteq P/C$. Thus the value of K may be obtained by plotting P/C against C. The intercept on the P/C ordinate gives the value of K.

Table I gives the values of φ as calculated from the osmotic pressure measurements.

TABLE I

C Gm/cc solution	P Mm Hg	P/C	$\varphi \times 10^2$	q Cc H_2O/Gm gelatin
0.0	—	325		
0.01	3.5	350	7.2	6.45
0.02	7.5	375	13.4	5.95
0.03	12.0	400	19.8	5.85
0.04	17.0	425	23.6	5.15
0.05	23.0	460	29.5	5.15
0.06	29.40	492	34.0	4.91
0.07	37.50	537	39.6	4.91
0.08	47.0	588	44.8	4.85

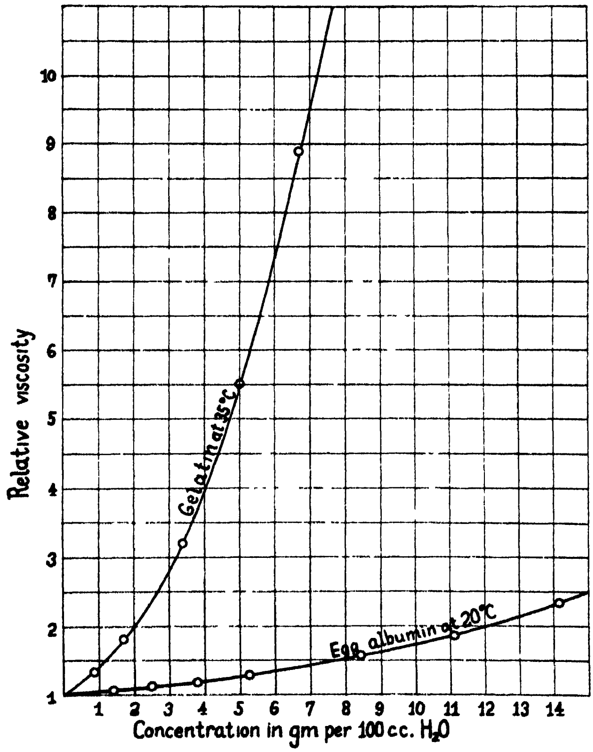

FIG. 4
Viscosity concentration curves of isoelectric gelatin at 35°C and of isoelectric egg albumin at 20°C.

The last column contains the values of the water of hydration per gram of gelatin as obtained from the values of φ, namely

$$q = \varphi/C - 0.75$$

where 0.75 equals the volume of 1 gram of dry gelatin.

Viscosity and Hydration of Gelatin.—The viscosity of a number of colloidal solutions, as well as of various sugar solutions, may be represented approximately by the empirical formula[10]

$$\eta = \frac{1 + 0.5\,\varphi}{(1 - \varphi)^4}$$

where η = relative viscosity of solution

and φ = volume occupied by the solute expressed as a fraction of the total volume of the solution = cc of solute per cc of solution.

In the case of various sugar solutions and also in the case of sulfur suspensions, the volume of the solute as calculated from the viscosity values agrees with the actual volume of the substance in the dry state, as determined from specific gravity measurements. In the case of hydrated or solvated substances φ represents the volume of the solvated solute. This was checked[10] for various colloidal solutions. Thus in the case of solutions of caoutchouc in benzene the values of φ as calculated from the viscosity measurements were found to fit remarkably well in the equation for osmotic pressure of the same solutions.

Table II shows the values for φ and hence also for q as calculated from the viscosity measurements of gelatin by means of the same formula.

TABLE II

C Gm/cc solution	η at 35°C.	$\varphi \times 10^2$	q Cc H_2O/Gm gelatin
0.01	1.43	7.75	7.00
0.02	2.06	15.05	6.78
0.03	2.96	21.80	6.52
0.04	4.24	27.90	6.30
0.05	6.00	33.40	5.93
0.06	8.20	38.10	5.60
0.07	10.85	42.18	5.28
0.08	13.9	45.52	4.94

The values for hydration of gelatin as obtained from the viscosity measurements are quite close to those obtained from the osmotic pressure measurement.

Figure 5 shows that when the various concentration values have been corrected for the values of φ as obtained from viscosity measurements the osmotic pressure values lie on a straight line.

It is to be noted that the value of water of hydration in cc per gm of gelatin becomes smaller as the concentration of gelatin increases. This agrees with the theory that the hydration of gelatin is due to the swelling of the micellae, owing to the difference between the osmotic pressure of the internal liquid phase and the osmotic pressure of the gelatin sol as a whole. The micellae swell until this difference in osmotic pressure becomes equal to the elastic resistance of the walls of the micellae.

The equilibrium state between the micellae and the total sol can be expressed as follows:

$$P_i - P_o = E_1 q$$

where P_i and P_o are the osmotic pressures inside and outside of the micellae, E_1 is a constant proportional to the bulk modulus of elasticity of the micellae and q is the amount of water held by the micellae (water of hydration) per gram of gelatin. At low concentrations of gelatin the outside osmotic pressure is much smaller than the osmotic pressure inside of the micellae, hence the micellae take up relatively large amounts of water. But as the total concentration of gelatin increases the opposing outside osmotic pressure increases and the micellae swell less with the result that q, *i.e.*, the amount of hydration per gram of gelatin, gradually becomes less and less. Thus, although the micellae are at equilibrium with the outside solution, they are still under an elastic stress exerted by a pressure equal to E_1 q, the magnitude of which decreases with the increase in the total concentration of gelatin. It is assumed that this elastic stress in the micellae is the cause of syneresis of gels, as will be described later.

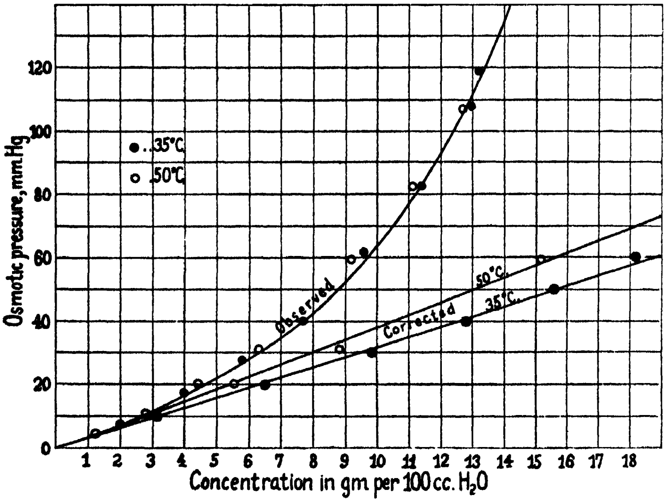

FIG. 5

Effect on the osmotic pressure-concentration curves of isoelectric gelatin of correcting the concentration of the gelatin for the water of hydration as calculated from viscosity measurements

Effect of Concentration of Gelatin on the pH—Viscosity Curves.

It is generally known that the addition of either acid or alkali to a freshly prepared gelatin sol raises its viscosity. In the presence of acid the viscosity reaches a maximum at pH 3.0 and then drops again. The pH effect on the viscosity of gelatin has been explained by Loeb as due to the swelling of the micellae in the gelatin sol. It is assumed that the micellae are of higher gelatin concentration than the total concentration of the gelatin in the outside solution; hence there is a greater concentration of acid in the micellae than in the solution outside of the micellae. It is this unequal distribution of the acid or alkali which causes the micellae to swell and hence brings about a rise in the viscosity of the gelatin sol. With increase in the total concentration of gelatin the difference in the concentrations of gelatin in the internal and external liquid phases and hence also the difference in the distribution of the ions of the acid or alkali is gradually diminished. At the same time the total osmotic pressure of the gelatin solution which opposes the swelling of the micellae is continually increased. Hence the increase in viscosity at pH 3.0 over that of isoelectric gelatin should become less conspicuous with increase in the total concentration of the gelatin sol. That this is exactly what happens is shown in Table III.

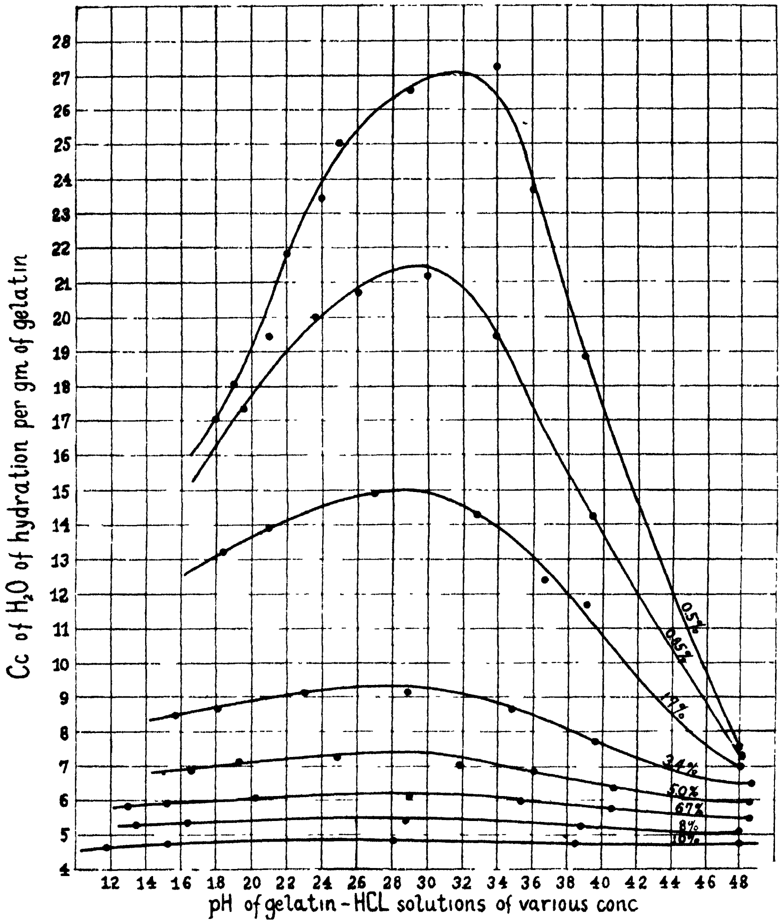

FIG. 6

Effect of concentration on the hydration of gelatin at various pH. The hydration values were calculated from viscosity measurements at 35°C by means of the formula $\eta = \frac{1+0.5\varphi}{(1-\varphi)^4}$

TABLE III

Viscosity Measurement of Various Concentrations of Gelatin pH 4.7 and pH 3.0 at 37°C

Concentration in gm per 100 cc solution	0.5	1.0	2.0	3.0	4.0
Relative viscosity of gelatin pH 4.7	1.16	1.43	1.95	2.75	3.83
Additional viscosity = relative viscosity − 1	0.16	0.43	0.95	1.75	2.83
Relative viscosity of gelatin pH 3.0	1.84	2.39	3.44	4.54	5.78
Additional viscosity	0.84	1.39	2.44	3.54	4.78
Ratio of additional viscosity, pH 3.0/pH 4.7	5.24	3.23	2.57	2.02	1.69

Concentration in gm per 100 cc solution	5.0	6.0	8.0	10.0
Relative viscosity of gelatin pH 4.7	5.28	6.70	12.40	21.3
Additional viscosity = relative viscosity − 1	4.28	5.70	11.40	20.3
Relative viscosity of gelatin pH 3.0	7.12	9.06	14.20	22.0
Additional viscosity	6.12	8.06	13.20	21.0
Ratio of additional viscosity, pH 3.0/pH 4.7	1.43	1.42	1.16	1.03

The effect of the concentration of the gelatin on the hydration of gelatin at various pH is shown in Fig. 6. The hydration values were obtained from viscosity measurements at 35°C of various concentrations of gelatin freshly made up to various pH by means of HCl. The curves show that at a concentration of gelatin of about 10 per cent the pH effect on the viscosity of the sol disappears entirely, which indicates that at this concentration, the concentrations of gelatin inside and outside of the micellae are equal so that the osmotic pressure in the micellae is completely balanced by the osmotic pressure of the total sol.

Swelling and Syneresis of Isoelectric Gelatin[11]

When gels containing various amounts of gelatin are placed in cold water or dilute buffer solution of the same pH as that of the isoelectric point of the gelatin the following results are obtained. Gels of a gelatin content of more than 10 per cent swell while those of less than 10 per cent lose water and shrink. A gel containing about 10 gm of gelatin per 100 cc of solution neither swells nor shrinks. This is shown in Fig. 7.

This striking difference in the behavior of gels of various gelatin content may be explained qualitatively and predicted quantitatively on the basis of the following assumptions:

1. Swelling in gels of concentrations above 10 per cent is caused by osmotic pressure of the "soluble" component of gelatin which exists in solution

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[11] Kunitz: J. Gen. Physiol., 12, 289 (1928).

in the liquid phase of the gel at a temperature even as low as 0°C. The amount of the dissolved component gelatin in the liquid phase, and hence the swelling, increases both with the total concentration of gelatin in the gel and with temperature.

2. Shrinking or syneresis in gels of a gelatin content of less than 10 per cent is caused by the elastic stress in the micellae of the gelatin sol before it was cooled and allowed to set. The elastic stress in the micellae is due to the osmotic pressure of the dissolved gelatin in the internal liquid phase in the micellae. But as the gelatin solution is cooled and allowed to set the dissolved gelatin in the micellae becomes insoluble and precipitates out. The force which kept the micellae stretched is thus diminished. This allows the elastic walls of the micellae to shrink and lose water. The shrinking of each individual micella brings about a contraction of the whole network with the result that water is expelled not only from the micellae but also from the spaces between the micellae and the whole block of gel loses weight. This process is most rapid when the gel is placed in contact with water, since the loss of water from a dry gel is slow owing to the resistance offered by the dry surface film. As stated before, the elastic stress in the micellae of a gelatin sol due to the inner osmotic pressure becomes less as the total concentration of the gelatin increases. Hence when the stress on the micellae is removed by the precipitation of inner liquid on cooling of the sol there is less contraction in the micellar network of concentrated gels than in the dilute ones.

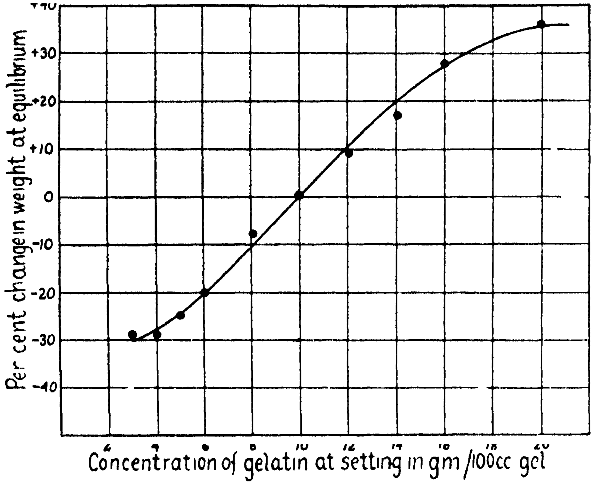

FIG. 7
Percentage change in weight of gels of various concentrations of isoelectric gelatin when placed in M/1000 acetate buffer pH 4.7 at 5°C

Thus while swelling increases with increase in concentration of gelatin in the gel, syneresis diminishes with the concentration. At a gelatin content of 10 per cent the force that causes swelling apparently balances the opposite force that causes syneresis or shrinking of the gel, and the gel neither swells nor shrinks.

3. A block of freshly set gel is under no elastic stress but becomes subjected to a tensile stress on swelling and to a compressive stress on shrinking, both forms of stresses being proportional to the amount of swelling or shrinking correspondingly. This is confirmed experimentally by double refraction measurements.[12] A block of gelatin at setting has no double refraction. A swollen block shows positive double refraction, corresponding to tension or stretching, while blocks which shrink show negative double refraction, corresponding to compression.

It follows therefore that both forces, namely the osmotic pressure of the liquid phase and the elastic stress in the micellae both of which tend to change the volume of the block, act against the elastic resistance of the block of gel. The amount of either swelling or shrinking of a gel depends then on the three forces, and at equilibrium we have

$$P_o - P_m = K\frac{V_e - V_o}{V_o} \qquad (1)$$

where P_o = osmotic pressure of liquid phase, P_m = pressure due to the stress in the micellae, K = bulk modulus of elasticity of the gel, both for tension and compression, V_o = volume of gel at setting, V_e = volume of gel at equilibrium. It is to be noted that $P_o - P_m$ represents the total swelling pressure of the gel.

The swelling pressures of gels of concentrations of higher than 10 per cent have been measured directly at 10°C and can be expressed approximately as the following function of V_e, where V_e is taken in cc of H_2O per gm of dry gelatin, namely

$$P_o - P_m = \frac{1330}{V_e} - 140 \qquad (2)$$

When $V_e = 9.5$ then $P_o - P_m = 0$

$V_e < 9.5$ " $P_o > P_m$

$V_e > 9.5$ " $P_o < P_m$

that is, at a concentration of 9.5 cc H_2O per gm of gelatin the gel exerts no swelling pressure; while at a lower concentration of gelatin, the swelling pressure becomes negative and the gel loses water, and at higher concentration the swelling pressure is positive and the gel swells.

Combining equations (1) and (2) we get an expression for the relation between V_o and V_e both expressed in cc H_2O per gm of gelatin, namely

$$\frac{1330}{V_e} - 140 = K\frac{V_e - V_o}{V_o}$$

which enables one to compute the amount of either swelling or shrinking of any gel if K is known.

This formula was found to hold quite well for the shrinking and swelling of a series of gels ranging in concentrations from 3 to 20 gm of gelatin in 100 cc of total volume. The smooth curve on Fig. 8 represents the equation while the dots are the observed values of the final concentrations of gelatin at equilibrium as plotted against the concentrations of gelatin at setting.

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[12] Kunitz: J. Gen. Physiol., **13**, 565 (1930).

The bulk modulus of elasticity as derived from the equation appears to be independent of the concentration of the gel, but it is difficult to say whether this fact has any theoretical significance. The curve for $P_o - P_m$ has been taken for simplicity as a straight line while the actual values are probably on a line which is convex downward. A curve of this form would result in a value of K which varied with the gelatin concentration, as is actually found to be the case when the relation between the swelling and the elastic stresses produced was determined by means of double refraction measurements.

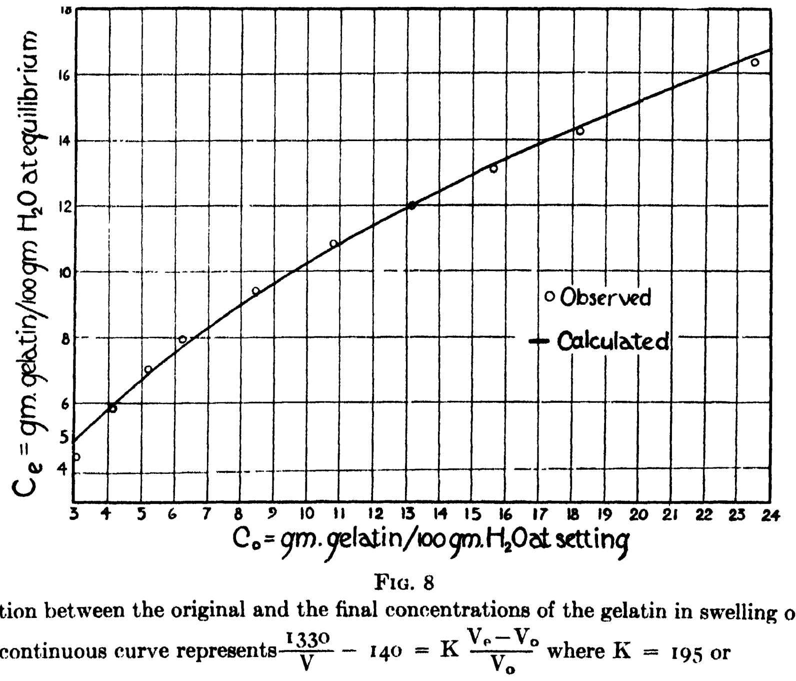

Fig. 8

Relation between the original and the final concentrations of the gelatin in swelling of gels. The continuous curve represents $\frac{1330}{V} - 140 = K \frac{V_e - V_o}{V_o}$ where $K = 195$ or

$C_e = \sqrt{4.28 + 14.66\, C_o} - 2.07$, $C_e = 100/V_e$, $C_o = 100/V_o$

Effect of Previous Treatment on Swelling[13] or Syneresis[11]

It follows from the preceding assumptions that the amount of swelling is determined by the concentration of the gelatin in the gel at the time of setting only and is not affected by subsequent drying or swelling at the same temperature, *i.e.*, a block which has been dried or swollen swells subsequently to the same final concentration as a block of the same original concentration placed directly in water.[14] It also follows that a block which has been dried or swollen is under elastic stress and should therefore show fatigue. If such a block is kept for some time at a low temperature or warmed for a short time, the elastic stress should decrease, owing to fatigue and the block should then behave in the same way as a block which solidifid at the corresponding concentration. This is the result observed.

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[13] Northrop: J. Gen. Physiol., **10**, 893; Northrop and Kunitz: 905 (1927).

[14] This behavior may undoubtedly be modified by the "case-hardening" effect described by Sheppard and Sweet.

The effect of temperature, and the size and shape of the block on the equilibrium and also on the rate of swelling may be quantitatively predicted by means of these assumptions.

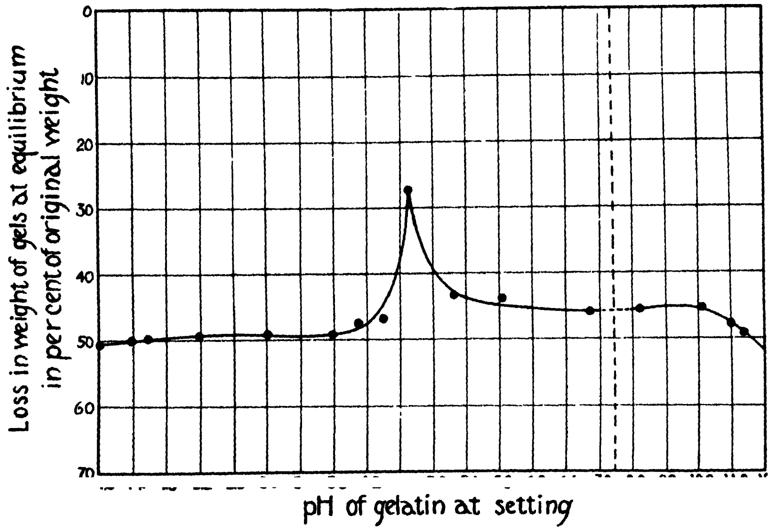

Fig. 9

Effect of pH on syneresis of 3 per cent gel in M/1000 acetate buffer pH 4.7 at 5°C.

Syneresis in Gels containing Acid or Alkali[11]

The amount of shrinking of dilute gels when placed in H_2O or dilute buffer both of pH about 4.7, depends not only on the concentration of gelatin but also on the pH and the electrolyte content of the gel before it was placed in H_2O or buffer solution. The effect of pH is shown in Fig. 9. It is seen that gels which had a pH other than that of the isoelectric point of gelatin lose more weight than gels made of isoelectric gelatin. The shrinking takes place only after the acid or alkali has been removed by neutralization and dialysis. The greater shrinking of gels which contained acid or alkali in solution at setting, over those which were electrolyte-free takes place only in gels of low gelatin content. The difference disappears in case of gels of concentrations above 6 per cent. The peculiar effect of the pH of the original solutions on the loss of water by the gels after the gel was brought back to the isoelectric point becomes clear on the basis of the micellar theory developed here. In dilute sols of gelatin containing moderate amounts of acid or alkali the micellae are much more swollen than at the isoelectric point due to a greater concentration of diffusible ions inside than outside of the micellae, and hence the micellae are under a greater elastic strain. Cooling and setting does not change this unequal distribution of ions. Hence, until the ions are removed by dialysis the micellae do not lose water and no syneresis takes place. But as soon as the acid or alkali is removed by neutralization and dialysis the micellae shrink much more than in the case of originally isoelectric gels. With increase in the concentration of gelatin the pH effect on the swelling of the micellae in a gelatin sol diminishes rapidly as shown by viscosity measurements, with the result that the pH effect on syneresis in the gels is also diminished with increase in concentration of the gelatin. There is also another factor in the effect of acid or alkali on syneresis, namely the solubility effect which is shown also by salts.

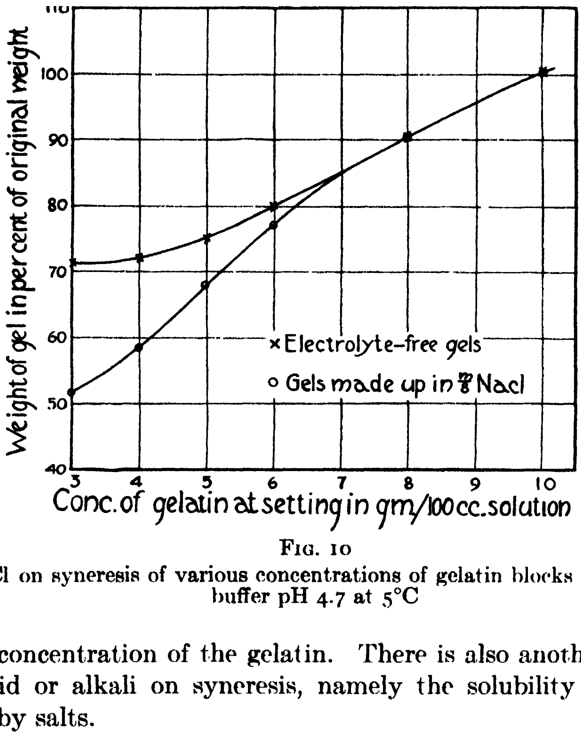

FIG. 10

Effect of NaCl on syneresis of various concentrations of gelatin blocks in M/1000 acetate buffer pH 4.7 at 5°C

The Effect of Salts on Syneresis[11]

The salt-containing gels of a gelatin content of less than 8 per cent are placed in large amounts of M/1000 acetate buffer pH 4.7 at 5°C the salt dialyzes out and the gels begin to lose water. But the amount of water lost in this case is considerably greater than in the case of electrolyte-free gels. This is shown in Fig. 10. Salt increases the solubility of gelatin, hence, in the presence of the salt, the gelatin in the micellae remains in solution instead of precipitating and the micellae do not shrink. But as soon as the salt is removed by dialysis the dissolved gelatin in the micellae precipitates out and the contraction and hence the loss of water results. The net result is therefore a greater loss of water due to syneresis in salt-containing gels than in salt-free gels of pH 4.7.

Acids and alkalies in addition to their pH effect on gelatin have also an enormous effect on the solubility of gelatin. A continuous increase in acid or alkali concentration has the same effect on the solubility of gelatin as addition of large amounts of salt, and at higher concentration of acid or alkali the solubility effect prevails. This explains why the curve for syneresis effect of pH does not show a maximum point as do the pH viscosity curves.

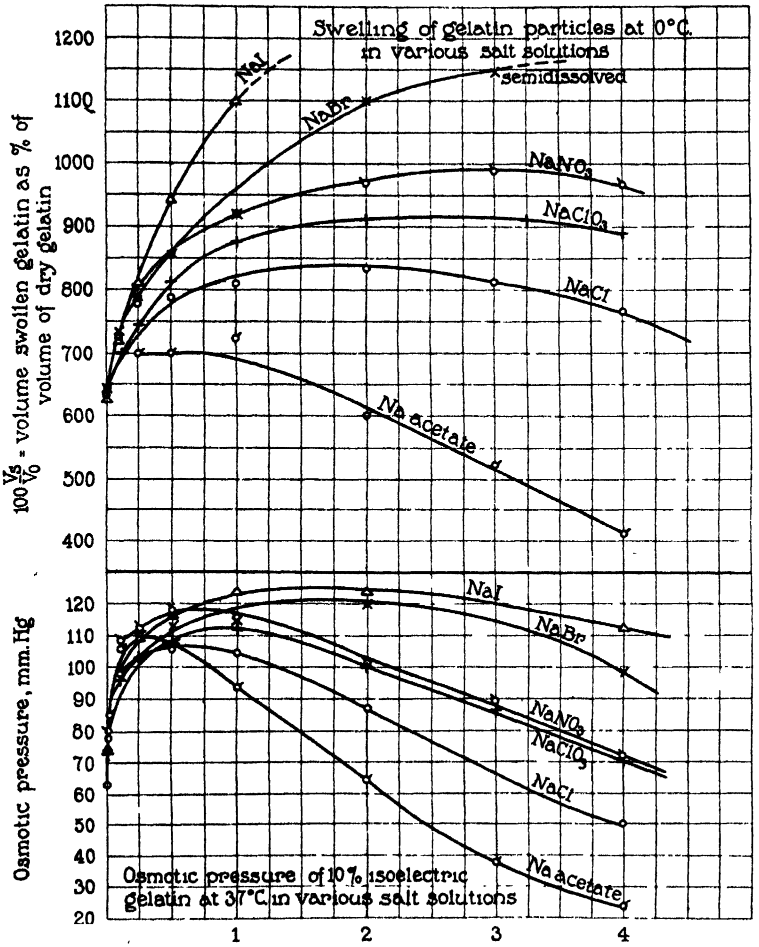

FIG. 11

Comparison of osmotic pressure and swelling of gelatin in various salt solutions

Osmotic Pressure and Swelling of Isoelectric Gelatin in Salt Solutions.[15]

The studies of Loeb have shown that the swelling and osmotic pressure of gelatin, caused by acid or alkali, is depressed by salts; the amount of depression increases with the concentration of the salt and also with the valency of either the anion or the cation, depending on whether the osmotic pressure (or swelling) was caused by acid or by alkali.

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[15] Northrop and Kunitz: J. Gen. Physiol., 8, 317 (1926).

The effect of salts on the osmotic pressure and swelling of isoelectric gelatin in the absence of acid or alkali is quite different. This is shown in Figs. 11 and 12. The curves show that salts usually increase both the osmotic pressure and the swelling of isoelectric gelatin, and the effectiveness of the

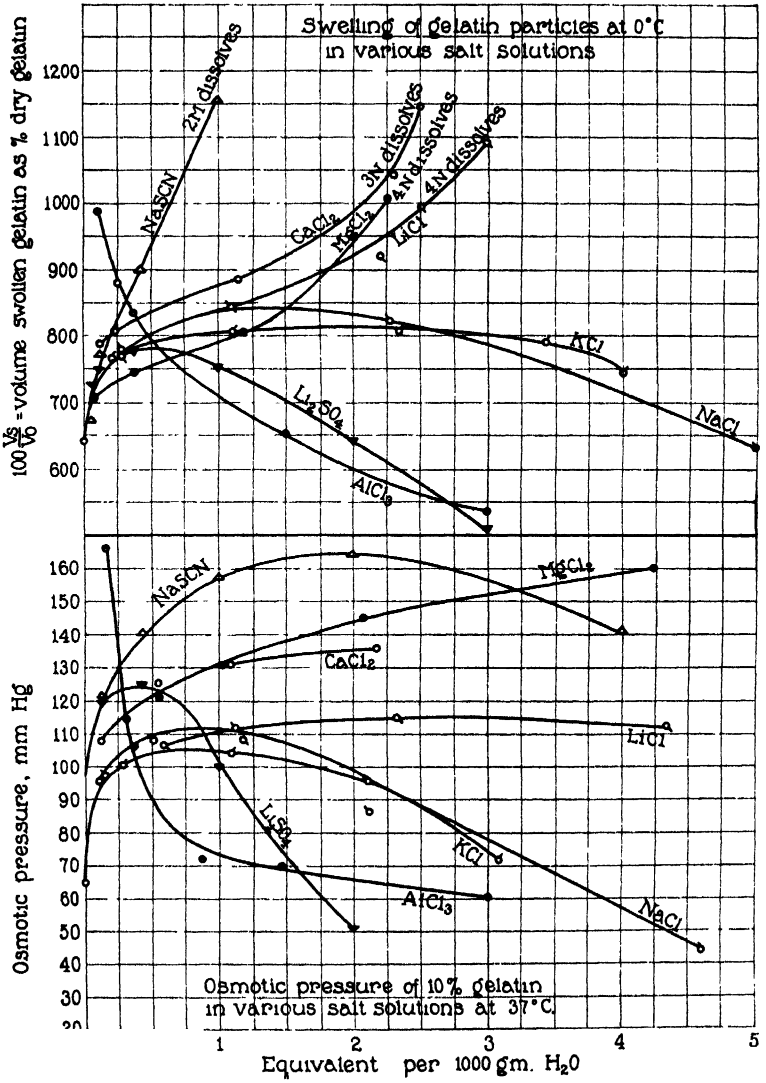

FIG. 12
Comparison of osmotic pressure and swelling of gelatin in various salt solutions

various salts here does not depend on the valency of the salts but on their chemical nature, so that the salts may be arranged in a series quite similar to the Hoffmeister series. The curves both for osmotic pressure and swelling run parallel throughout a wide range of concentrations of salt, which shows that the increase in the amount of swelling of isoelectric gelatin caused by salt is due primarily to an increase in the osmotic pressure of the gelatin. Some salts such as aluminum chloride raise the osmotic pressure of gelatin through the formation of non-diffusible complex ions between the gelatin and one of the ions of the salt, and thus are able to set up a Donnan equilibrium. But most salts raise the osmotic pressure by splitting the micellae into smaller units. This follows from the experimental fact that salts affect only slightly the osmotic pressure of the soluble component of gelatin, while the osmotic pressure of the insoluble fraction of gelatin is increased enormously by salts. This is shown in Table IV. In the case of gels the swelling pressure is greater in the presence of salt for the reason that salts increase the concentration of dissolved gelatin in the liquid phase.

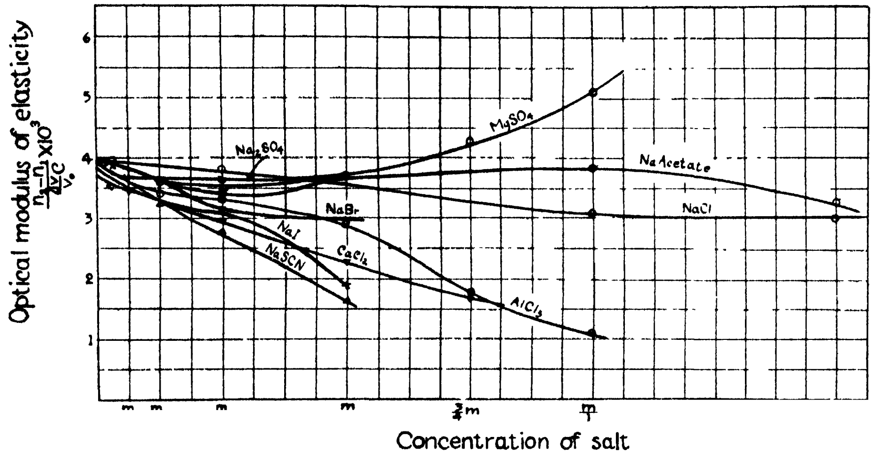

FIG. 13

The effect of salts on the elasticity of 10 per cent gels as calculated from double refraction measurements

TABLE IV

Effect of NaSCN on the Osmotic Pressure of 5 Per Cent Soluble and Insoluble Fractions of Gelatin at 37°

Fraction	Soluble		Insoluble	
Concentration of NaSCN inside and outside	0	2M	0	2M
Osmotic pressure, mm Hg	50	61	8	35

In high concentration salts begin to affect the bulk modulus of elasticity of the block of gel. This is especially true of such salts as $CaCl_2$, NaSCN, NaI, and LiCl. In the case of these salts the parallelism between the osmotic pressure and swelling curves holds only for low concentration; at concentra-

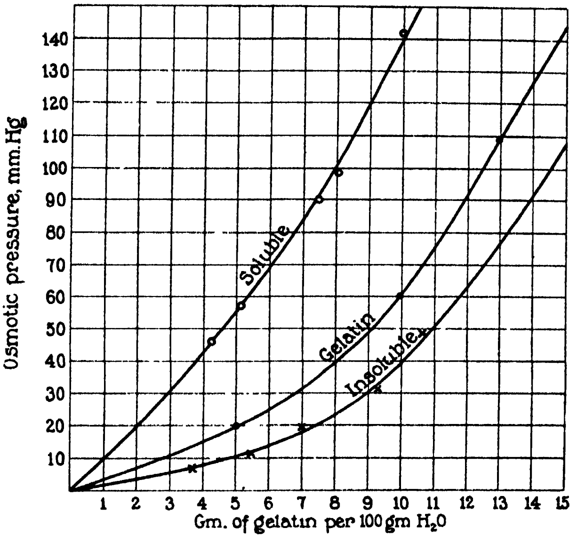

FIG. 14

Osmotic pressure at 37°C of various concentrations of isoelectric gelatin and of the soluble and insoluble fractions

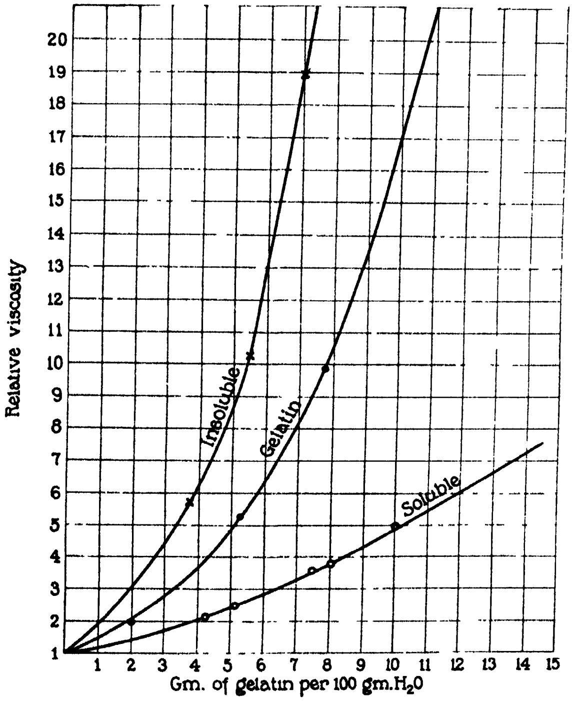

FIG. 15

Viscosity at 37°C of various concentrations of isoelectric gelatin and of the soluble and insoluble fractions

tions above M/2 the osmotic pressure curves begin to drop with increase in concentration of salt, while the swelling curves continue to rise, owing to the rapid drop in the elasticity of the gel, until the gels become too soft to stand any swelling pressure and fall apart (dissolve) completely in very high concentrations of these salts.

A detailed study of the effect of salts on the elastic properties of gelatin during swelling was made[12] by means of double refraction measurements and the results are shown in Fig. 13.

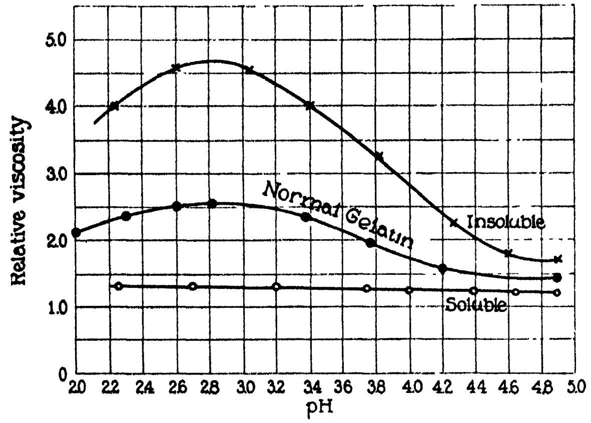

FIG. 16

Effect of addition of HCl on the viscosity at 37°C of 1 per cent solutions of isoelectric gelatin and of the soluble and insoluble fractions

In concentration below M/8 most of the salts investigated have practically no effect on the elasticity of gelatin, while above M/8 salts like NaSCN, NaI, or $CaCl_2$ bring about a rapid decrease in the modulus of elasticity of the gels with increase in the concentration of the salts.

Fractionation of Gelatin[16]

If gelatin really consists of two components it should be possible to separate them at least partly and further the fractions should have very different properties. The "soluble" fraction should have high osmotic pressure, low viscosity and the viscosity should not change much with the addition of acid or alkali since it contains no micellae. The "insoluble" fraction should have very low osmotic pressure, very high viscosity and the viscosity should vary markedly with the pH since it contains a larger percentage of micellae than the original gelatin. The "insoluble" fraction should not swell much in H_2O and mixtures of the two fractions should swell more the larger the percent of soluble fraction. The "insoluble" fraction should swell in acid or alkali.

Schryver[17] and his associates found that gelatin could be fractionated by allowing dilute isoelectric gelatin solutions to set. Syneresis occurs under these conditions and a soluble compound is found in the filtrate. This observation was repeated and confirmed by the writers and a "soluble" and "insoluble" fraction prepared by a modification of Schryver's method. These fractions had the properties predicted as shown in Figs. 14 to 17.

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[16] Northrop and Kunitz: J. Gen. Physiol., **10**, 167 (1927); **12**, 379 (1929).

[17] Biochem J., **17**, 473 (1923).

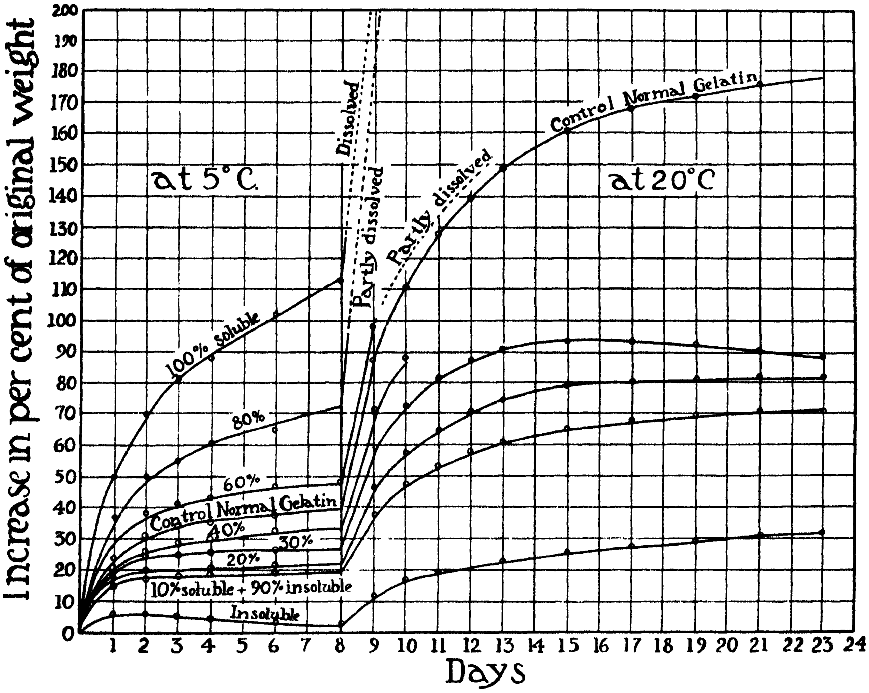

FIG. 17
Swelling of 30 per cent gels consisting of mixtures of insoluble and soluble fractions of gelatin. Blocks of gel weighing about 1.5 gm each were allowed to swell in 200 cc M/30 acetate buffer pH 4.7

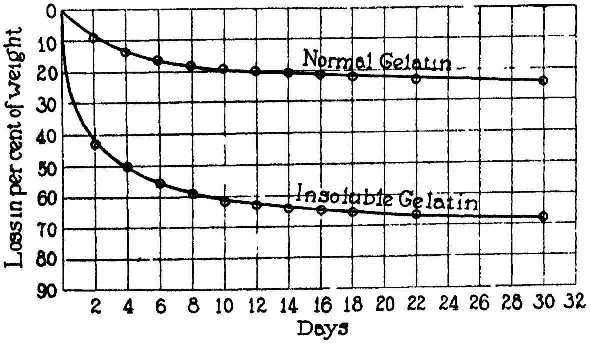

FIG. 18
Syneresis of 5 per cent gels in M/30 acetate buffer pH 4.7 at 5° C

The presence of two components in gelatin gels has been deduced by Trillat[18] from X-ray studies.

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[18] Compt. rend., 190, 265 (1930).

Syneresis of Dilute Gels of "Insoluble" Gelatin[19]

In ordinary gelatin the micellae form only a part of the total gelatin, the rest of which is found in solution outside of the micellae. A solution of the "insoluble" fraction of gelatin in dilute NaOH, on the other hand, consists nearly completely of a dispersion of swollen micellae, as shown by the high viscosity of such a solution. Hence it would be expected that a dilute gel made of the "insoluble" gelatin should lose more water when put in dilute buffer pH 4.7 than a corresponding gel made from ordinary gelatin. That this is actually what happens is shown in Fig. 18 where the curves for the rate of shrinking of the 5 per cent gels made of ordinary gelatin and of the "insoluble" fraction of gelatin are given.

Summary

The swelling, osmotic pressure, viscosity and syneresis of gelatin gels or sols may be quantitatively accounted for on the following assumptions.

Gelatin sols or gels are two-phase, three-component systems. The solid phase consists of particles (micellae) of an insoluble ingredient of the gelatin. The liquid phase is an aqueous solution of the "insoluble" fraction and of a "soluble" fraction in water.

Each micella is a separate system consisting of an insoluble, elastic wall or network containing an "internal" liquid phase. This "internal" liquid phase is a solution of the "insoluble" fraction forming the wall of the micella and of one or more other fractions which have a high temperature coefficient of solubility and for which the walls of the micellae are impermeable.

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[19] Kunitz and Northrop: J. Gen. Physiol., **12**, 379 (1929).

THE REVERSIBILITY OF PROTEIN COAGULATION

BY M. L. ANSON AND A. E. MIRSKY

Coagulation is the most striking reaction of the proteins. For ages it has been a familiar phenomenon because of the prominent rôle it plays in cookery. The change occurring in egg-white when an egg is immersed in boiling water shows how conspicuous protein coagulation can be. Indeed, with combustion and fermentation, protein coagulation was one of the first chemical processes recognized by man. It was only natural, therefore, that this process should early have attracted those interested in the chemical study of living phenomena. For several hundred years the recognition in plant and animal tissues of what is now called protein depended on its property of coagulating when heated. The result of this was that during the nineteenth century there was widespread among biologists and biochemists an acquaintance with even some of the minor details of protein coagulation. More recently, however, there has been a tendency among biologists to neglect the study of protein coagulation, for it has been supposed that coagulation is a degradation process, that coagulated protein is an early stage in the disintegration of the protein molecule, and finally that coagulation, being irreversible, can be of little physiological interest. Investigation of the acid-base properties of proteins appeared to be of greater physiological significance, so that many physiologists are now familiar with protein properties that can be detected only with refined methods, while they are hardly acquainted with some of the gross, easily-recognizable properties. For the investigator of biological function it is an important difference between the acid-base properties and those associated with coagulation that whereas the former are common to many substances, the latter appear to be unique, peculiar to proteins. If it could be shown that protein coagulation is reversible, its biological significance would be greatly enhanced.

Description of Coagulation. The coagulation of a protein occurs in two distinct steps:[1] first, a chemical change in the protein and second, precipitation of the altered protein. In the first step, the protein is so modified(whether by heat, acid, alkali, alcohol, or a number of other agents) that it is no longer soluble under conditions under which the original protein is soluble. Whereas the original protein is soluble at its isoelectric point, modified protein is insoluble at the isoelectric point. Addition of acid or alkali dissolves modified protein. The process whereby the original, or *native*, protein is changed is called *denaturation* and the changed protein is called a *denatured protein.* The distinctness of the two steps of coagulation is apparent when denaturation occurs at a hydrogen ion concentration removed from the protein's isoelectric point, for under these conditions even after prolonged heating, no visible change may be noticed. Denaturation has, however, taken place, and the denatured protein has remained in solution, as can be shown by adjusting the hydrogen ion concentration to the isoelectric point, whereupon denatured protein precipitates. Although the second step in coagulation, precipitation of denatured protein, is readily reversible, the first step, denaturation, has been generally supposed to be irreversible.

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[1] Chick and Martin: J. Physiol., **40**, 404 (1910); **43**, 1 (1911).

Flocculation of denatured protein depends primarily upon the change on the protein particles and is therefore probably analogous to the coagulation of colloids in general. Denaturation, on the other hand, is a process peculiar to proteins and should not be confused with the ordinary coagulation of colloids. Investigation of the kinetics of denaturation[1] shows it to be a process following the course of a unimolecular reaction, the velocity of which is increased about 600 times when the temperature is raised 10°C. Denaturation may therefore be slow at one temperature and rapid at a temperature only a few degrees higher. This is the reason why proteins appear to have a definite temperature of coagulation. Perhaps this remarkable temperature coefficient of denaturation will arrest the attention of chemists who may know of some analogous reaction; at present it appears to be unique. It has accordingly been used to detect the rôle of protein in certain processes. When, for instance, bacteria are killed by heat, the process has a temperature coefficient of about 600 for 10°C, indicating that heat causes death in bacteria by denaturing certain bacterial proteins.[2] The inactivation of some enzymes by heat has a temperature coefficient of 600 for 10°C, indicating that denaturing a protein destroys enzymatic activity and that protein is probably part of the enzyme molecule. For crystalline pepsin this has been more directly demonstrated, for its loss of activity is quantitatively paralleled by its denaturation.[3]

A chemist will at once ask what structural changes occur in denaturation. The process has been followed mainly by physico-chemical observations, particularly by the gross change in solubility, and little is known of the underlying structural changes. In addition to the change in solubility it has been observed that denaturation causes a large increase in viscosity, a slight change, if any, in acid-base properties,[4] and, apparently, the loss of ability to crystallize. In the case of hemoglobin the changes are especially conspicuous, for denaturation of globin, indirectly affecting the heme to which it is attached, causes a marked change in color and absorption spectrum and loss of the ability of heme to combine loosely with oxygen. It is not known what modifications in the chemical groups of globin bring about these changes. The only definite structural changes known to accompany denaturation are in the sulfhydryl groups.[5] The presence of sulfhydryl groups can be demonstrated in denatured egg albumin by means of color reactions and oxidation-reduction reactions. When native egg albumin is examined by the same methods these sulfhydryl groups cannot be detected. The same, or a similar

[2] Chick: J. Hygiene, **10**, 237 (1910).

[3] Northrop, J. Gen. Physiol. **13**, 739(1930).

[4] Booth: Biochem. J., **24**, 158 (1930).

[5] Arnold: Z. physiol. Chem., **70**, 300 (1910).

difference, can be demonstrated between the native and denatured forms of other proteins. We are now making a quantitative study of protein sulfhydryl groups.

The Supposed Irreversibility of Coagulation. Ever since coagulation has been studied at all, it has been taken as almost axiomatic that coagulation is irreversible. Usually coagulation has been thought to be the first step in the degradation, the breaking down of the protein. As a result, in the study of the chemistry of the normal, native protein coagulation has been considered something to be avoided. And in discussions of the physiological rôle of the proteins, coagulation has hardly been mentioned. It is true that procedures which result in the denaturation of proteins also result in their degradation. Heat, which denatures proteins, also splits off ammonia. Acid which denatures proteins also splits off amino acids. Were such changes an inherent part of denaturation, then obviously reversal of denaturation would be impossible. But, as the Sörensens[6] showed, the splitting off of ammonia by heat has nothing to do with denaturation. It is a secondary change in the protein which takes place slowly when the protein is heated after it has already been denatured. In general, there is no evidence in any case that the decomposition caused by denaturation procedures is anything but a secondary reaction which is entirely separate from denaturation itself. Reversal of denaturation cannot, therefore, be excluded as impossible on the *a priori* ground that denaturation involves decomposition.

The only evidence that denaturation is irreversible has been that denaturation could not be reversed. It has long been familiar, for instance, that if an acid or alkaline solution of denatured egg albumin is brought to the isoelectric point of egg albumin, all the protein precipitates. Indeed, whatever one does to denatured egg albumin apparently one cannot prepare native egg albumin from it again. This negative result might mean that denaturation cannot be reversed. But it might also mean merely that egg albumin is unsuitable material for the experiment, that denaturation can be reversed only with difficulty, or that a special technique is required.

The Reversal of the Coagulation of Hemoglobin. Our experiments[7] on the reversibility of coagulation had their origin in a simple but inconclusive experiment with hemoglobin. An alkaline solution of denatured hemoglobin was neutralized. Practically all the protein precipitated, but (as is not the case with egg albumin) a small fraction of the protein remained in solution. Consequently, the supernatant solution was slightly colored whereas when a precipitate of denatured hemoglobin is shaken with water, the water remains colorless. Furthermore, the spectrum of native hemoglobin is entirely different from that of denatured hemoglobin and the small amount of protein in the supernatant solution had unmistakably the spectrum of native hemoglobin. Either this small amount of hemoglobin had escaped denaturation in the first place or the coagulation of hemoglobin had been partially reversed.

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[6] Sorensen and Sörensen: C. r. Trav. Lab. Carlsberg, **15**, No. 9, 1 (1925).

[7] Anson and Mirsky: J. Physiol., **60**, 50 (1925); J. Gen. Physiol., **9**, 169 (1925); **12**, 273 1928; **13**, 121, 133, 469, 477 (1930); Physiol. Rev., **10**, 506 (1930).

The explanation of the result on the basis of incomplete coagulation became unlikely when, with improvement in technique, it became possible to convert not a few per cent but two-thirds and more of the coagulated hemoglobin into a protein with the characteristics of native hemoglobin. Such "reversed" hemoglobin is soluble, coagulable, and crystallizable. It has the spectrum of native hemoglobin and can combine loosely with oxygen.

The technique of the experiments is simple. It consists in reversing the denaturation procedure by neutralizing an acid solution in two steps. Hemoglobin is readily denatured by acid. If an acid solution is rapidly and completely neutralized, that is, brought to the isoelectric point of the protein, then practically all the insoluble, denatured protein is precipitated. In fact, denatured hemoglobin is insoluble not only at its isoelectric point but in a wide region around its isoelectric point. If, however, the acid solution is not completely neutralized in one step, but is brought to the edge of the precipitation zone by adding just insufficient alkali to cause precipitation, then if, after a time, more alkali is added to complete the neutralization, only about a third of the protein is precipitated. The rest seems to be native hemoglobin. Similarly, if just enough alkali is added to make the solution just alkaline enough to prevent precipitation, then if, after a time, the solution is neutralized by the addition of acid, only a fraction of protein is precipitated.

All these reactions can be followed with peculiar ease in the case of hemoglobin because hemoglobin is a pigment. The color of the solution tells immediately about how much protein it contains. The spectrum of the solution tells whether the protein is native or denatured. Hemoglobin consists of a colorless protein, globin, joined to an iron pyrrol pigment, heme. In the blood, hemoglobin transports molecular oxygen from the lungs to the tissues. Heme itself could not act as a carrier of oxygen. It is not soluble enough and it does not combine loosely with oxygen in the way hemoglobin does. It is by combination with globin that heme is modified to give hemoglobin its valuable biological properties. The globin must be native. The compound of heme with denatured globin (called globin hemochromogen and possessing its own type of spectrum) is not soluble in water and does not combine loosely with oxygen.

Changes, then, such as denaturation of globin to which heme is attached in hemoglobin, are reflected in changes of the properties of heme, particularly in the spectroscopic properties which are readily and accurately followed. Heme in hemoglobin may therefore be used as a convenient and sensitive indicator of what is happening to globin. Just as globin influences heme with which it is combined, however, heme also influences globin, for instance by influencing the ease of its denaturation and the reversal of this denaturation. *A priori* it might even be true that the experiments on the coagulation of hemoglobin which have been described are concerned not with the general properties of the coagulable proteins but with the peculiarities of hemoglobin, peculiarities due to the effects of heme on globin. All the available experimental evidence, however, indicates that the results obtained from the study of the coagulation of hemoglobin are entirely general.

In the first place, in all the ways which have been tried hemoglobin behaves like a typical coagulable protein. All the procedures such as heating, exposure to ultra-violet light and to high pressure, shaking, adding acid, alkali, alcohol, acetone, urea or thiocyanate, which convert egg albumin into an insoluble denatured protein have the same effect on hemoglobin. The heat coagulation of hemoglobin like that of egg albumin obeys the equation of a unimolecular reaction and has the extraordinary temperature coefficient of over 600. And denatured hemoglobin has the same general properties as denatured egg albumin.

The Reversal of the Coagulation of other Proteins. The most convincing evidence that the hemoglobin reactions are not due simply to the presence of heme is that precisely the same experiments can be carried out even in the absence of heme. Colorless globin itself behaves just like hemoglobin. If an acid solution of denatured globin is rapidly and completely neutralized in one step, then practically all the protein is precipitated, especially if there is salt in the solution. If the two-step procedure is used, however, then a large yield of soluble, coagulable protein is obtained. With serum albumin the experiments are even easier. Denatured serum albumin is soluble except *exactly* at its isoelectric point or in the presence of concentrated ammonium sulfate. In neutralizing a solution of denatured serum albumin unless one has been very careful to secure the correct hydrogen ion concentration one does not observe any precipitate at all. To obtain from denatured serum albumin a large yield of albumin which is soluble even in concentrated salt solution it is not necessary to neutralize in two steps. Simple, complete neutralization in one step suffices. One need not even let the solution stand before making the test for native protein. In fact, it is hard in neutralization experiments with denatured serum albumin to avoid the reversal of coagulation. So long ago as 1910, Michaelis and Rona[8] probably observed reversal. Unfortunately, there was some confusion at the time about two different kinds of coagulation. And the test for denatured serum albumin was uncertain. As a result, these experiments never received the attention they deserved. Later (at the same time as our hemoglobin experiments) Spiegel-Adolf[9] gave good physicochemical evidence of the reversibility of the coagulation of serum albumin. More recently (unpublished experiments) we have studied serum albumin in a somewhat different way and have succeeded in obtaining from coagulated serum albumin, crystals of soluble coagulable protein in any desired amount.

With egg albumin, no great amount of reversal has resulted from any procedure so far tried, a result in harmony with previous experience. Just as the great ease of reversal in the case of serum albumin seems to be associated with the great solubility of denatured serum albumin, so in the case of egg albumin the difficulty of reversal seems to be associated with the great insolubility of denatured egg albumin. Denatured egg albumin not only is insoluble over a wide range of hydrogen ion concentration around its isoelectric point, but even beyond the zone of visible precipitation, it has a great tendency to form invisible aggregates (unpublished experiments). This is readily shown by viscosity measurements. In fact, the conditions for reversal in the case of other proteins are, in the case of egg albumin, the conditions for gel formation. It is possible to obtain a clear gel from a solution of denatured egg albumin containing only a half a per cent of protein.

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[8] Biochem. Z., 29, 494 (1910).

[9] Biochem. Z., 170, 126 (1926).

The ease of reversal then, varies from one protein to another; from one hemoglobin derivative to another; from the hemoglobin of one species to that of another; from serum albumin to egg albumin. Such differences in the ease of reversal are not surprising since, as is well known, there are similar differences in the ease of denaturation. Where reversal is possible, it is brought about by keeping the protein for a time in a solution that is beyond the precipitation or aggregation zone and yet not too far from the isoelectric point. With denatured egg albumin it does not seem possible to realize such conditions.

It remains to describe the more detailed evidence in favor of the reversibility of coagulation. Clearly it is not sufficient to obtain from a protein which seems to be denatured a protein which seems to be native. There must be adequate tests for the completeness of the coagulation and for the identity of the protein obtained from the coagulated protein with the original native protein. To obtain *completely* conclusive results is at present impossible. Not enough is known either about the changes involved in denaturation or about the means of characterizing completely a native protein.

Evidence of the Completeness of Coagulation. Since the most conspicuous change associated with denaturation is the change in solubility, the most obvious test for complete denaturation is insolubility. This test has been made in all cases. Usually an acid solution was rapidly neutralized with resulting complete precipitation of the protein. In one experiment, it was possible to test for insolubility under exactly the conditions under which reversal took place. To an acid solution of denatured hemoglobin there was added an excess of alkali just sufficient to keep the protein in solution. If this solution was half saturated with ammonium sulfate *immediately*, practically all the protein was precipitated. The later the salt was added, the less protein was precipitated. Finally, two-thirds of the protein remained in solution. In other words, denatured hemoglobin originally brought into slightly alkaline solution was insoluble in half saturated ammonium sulfate. With time it gradually changed into another form which like native hemoglobin was soluble.

It might be objected that precipitation at the isoelectric point is not an adequate test for insolubility or denaturation. *Conceivably*, when a denatured protein is precipitated it *might* carry down any native protein present. To explain reversal on this basis one must assume that only one-third the protein is denatured and that this third, when precipitated carries with it two-thirds which escapes denaturation. Experimentally, however, there is as yet no evidence that this can take place. If one prepares a known mixture of native and denatured hemoglobin or globin and precipitates the denatured protein, the concentration of native protein in the solution is not changed.

About the same yield of soluble protein is obtained from denatured protein if it is left in acid three minutes or eighteen hours; if it is heated, or left in acid, or heated in acid at two different temperatures; if it is denatured by urea, or trichloracetic acid, or 90 per cent acetone containing acid. If obtaining soluble protein were simply an indication of incomplete denaturation the yields ought to vary enormously with the time to which the protein is subjected to the denaturation procedure and with the nature of the denaturation procedure. The only alternative conclusion is that complete denaturation is impossible with the ordinary procedures.

In the case of denaturation by urea, it is possible to follow the course of denaturation by viscosity measurements. Concentrated urea solutions denature proteins slowly and also keep denatured proteins in solution, even at the isoelectric point. As the protein remains in the urea solution, more and more of it is converted into a form which is insoluble in the absence of urea. Associated with this formation of insoluble, denatured protein there is a gradual increase in the viscosity of the urea solution. Finally, all the protein is precipitated if the urea is removed. From this time on there is no further change in the viscosity. The hemoglobin precipitate formed by removing the urea after the viscosity has ceased to change may be largely reconverted by the reversal procedure into soluble, coagulable protein.

Lastly, we have recently been testing the completeness of denaturation by measuring the extent of specific group changes.

Evidence of the Completeness of Reversal. In all, then, the evidence so far obtained indicates that the experiments on the reversibility of coagulation have been started with completely coagulated protein, that at least no significant part of the soluble protein finally obtained is derived from protein which never was denatured. To complete the proof of the reversibility of coagulation it must be shown that the soluble protein finally obtained is the same as the native protein originally coagulated. It might be true that some soluble fraction was extracted from the coagulated protein, or that some parts of coagulation were reversed—enough to give a soluble protein—but that the "reversed" protein was still quite different quantitatively from the original protein.

Normal hemoglobin and "reversed" hemoglobin have accordingly been compared in quite a number of ways, some of them possible only because of the presence of heme in the molecule as an indicator. In the first place "reversed" hemoglobin is not only soluble, but it can by heating be coagulated again. The temperature of coagulation is exactly the same as that of normal hemoglobin. Similarly "reversed" hemoglobin can be crystallized (no denatured protein has yet been crystallized) and the crystals to the unaided eye seem to have the same form as those of normal hemoglobin. Precise crystallographic measurements have not been made. The spectrum of "reversed" hemoglobin has the same pattern as that of normal hemoglobin. The bands are in the same positions within the small experimental error of two Ångström units. Furthermore, "reversed" hemoglobin can be converted into pigments having the same characteristic spectra as the derivatives of normal hemoglobin. "Reversed" hemoglobin, like normal hemoglobin but unlike denatured hemoglobin, can combine loosely with oxygen. It has less affinity for oxygen than for carbon monoxide and the ratio of the two affinities is the same as in the case of normal hemoglobin.

The tests which have just been described are sensitive enough to distinguish readily between the slightly different hemoglobins of different mammals. Yet they cannot distinguish between "reversed" and normal hemoglobin. It is interesting to notice that although the spectra of the different *native* hemoglobins are measurably different, the spectra of the different *denatured* hemoglobins are not measurably different. This is in harmony with immunological experiments which show a decrease in species specificity on denaturation. When the denaturation of the different hemoglobins is reversed, the original spectra and hence the original spectral specificities reappear.

The comparison of "reversed" globin with normal globin cannot be undertaken at present because there is not yet available any certainly normal globin. The separation of globin and heme by present procedures seems to involve the denaturation of the protein. Hill and Holden[10] believed that they obtained native globin directly from hemoglobin. But no evidence was given in support of this claim. One can, however, synthesize hemoglobin from "reversed" globin and heme and compare the synthetic with normal hemoglobin. We have crystallized synthetic methemoglobin and carbon monoxide hemoglobin but the comparison with normal hemoglobin has not yet been completed.

The native globin of hemoglobin obviously has specific chemical groups with which it combines with heme to form hemoglobin. Denatured globin does not have these groups. At any rate, it cannot combine with heme to form hemoglobin, a substance with the characteristic spectrum and other properties of native hemoglobin. "Reversed" globin can once more form hemoglobin. There is reversal, then, as tested by examination not only of the physical but also of the specific chemical properties of the protein. Recently, we have also been measuring the thiol groups of native and denatured globin and serum albumin to see whether there is reversal of the characteristic changes in these groups.

So far, then, no difference has been found between normal and "reversed" protein. It is, of course, possible that differences might be found were the tests which have been used made more accurate or were other tests used. There is always the difficulty that since it is not known precisely what changes take place in denaturation, it is not known what differences might conceivably exist between normal and "reversed" protein. The most general sort of test which we have been applying recently is the solubility test. If native and "reversed" proteins are different, regardless of the nature of the difference, then their solubilities should be different.

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[10] Biochem. J., **21**, 625 (1927).

We may summarize the experiments on the reversal of coagulation in the following manner: If an acid solution of denatured egg albumin is neutralized, all the protein is precipitated, the denaturation of egg albumin being *apparently* irreversible just as has always been supposed; but if hemoglobin, globin or serum albumin is denatured by the ordinary procedures, one can, by a suitable technique, obtain from these insoluble denatured proteins, soluble, coagulable proteins which seem to be the same as the original native proteins. Experiments not yet completed or others not yet attempted may change the present conception of denaturation or disclose differences between native and "reversed" proteins. So far as the present evidence permits a conclusion, however, coagulation seems to be reversible. The only reason there ever was for believing coagulation to be irreversible, namely that coagulation could not be reversed, no longer has an adequate experimental basis. If the theory of the irreversibility of coagulation is still to be supported, it must be on the basis of new experiments, experiments which explain the results obtained with hemoglobin, globin and serum albumin.

The Biological Significance of Coagulation. It is a familiar fact that the solid matter of living active tissue consists mainly of coagulable proteins. Denaturation produces gross changes in the properties of proteins. Denaturation seems to be reversible. With these considerations in mind, it is difficult to believe that Nature has not exploited the coagulability of proteins. It is, for the moment, a tempting hypothesis that denaturation and its reversal are biological reactions which are important in ordinary cellular processes. It is this hypothesis at any rate which has led us to the study of the tissue proteins from the standpoint of coagulation. One wants to know whether the coagulation of the tissue proteins can be reversed, what group changes accompany this coagulation, how these changes can be studied under physiological conditions, and what is the nature of their function.

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THE EQUILIBRIUM BETWEEN GLYCOGEN AND LACTIC ACID*

BY WILDER D. BANCROFT AND GEORGE BANCROFT**

Otto Meyerhof, Warburg, A. V. Hill, and others have done considerable work in the last fifteen years on the formation and disappearance of lactic acid in muscles. They find that under anaerobic conditions, that is, in the absence of oxygen, lactic acid is formed from glycogen when the muscle is stimulated. They point out that the amount of lactic acid produced depends on the amount of work done by the muscle so that, in reality, the lactic acid is a measure of the work done. When the muscle is resting after a stimulation, oxygen is absorbed, producing aerobic conditions; part of the lactic acid is burned and part is converted back into glycogen. They assume that this oxidation and synthesis is a coupled reaction; the synthesis cannot take place in the absence of the oxidation which supplies the energy for it. The extent of this coupled reaction is remarkable, for Hill has shown that under suitable conditions the ratio of the amount oxidized to the amount synthesized is one to five or one to six. Such a large ratio is unprecedented, for no coupled reaction of this extent is known in chemistry. In cancer, where there is little accumulation of glycogen in the aerobic phase, this coupled reaction is still assumed to hold; but they believe in this case that the glycogen is broken down nearly as fast as it is formed, so that there is little accumulation. If the resting muscle is stimulated in oxygen and then allowed to rest, there is exactly the same result; part is burned and part of the lactic acid is converted back into glycogen again. There is however the difference that, during the stimulation, less lactic acid is formed in oxygen than in its absence. They assume that this is due to the recovery processes, oxidation and synthesis, going on simultaneously with the stimulation.

It is our purpose in this paper to show that the formation and disappearance of lactic acid in the muscle can be explained equally as well and in many instances better by the assumption that there is an equilibrium between glycogen and lactic acid in the muscle and that this equilibrium is reached by means of enzymes. The equilibrium point of this reaction is well over on the lactic acid side. As we shall see later, the reaction can be forced back from lactic acid to glycogen by the adsorption of glycogen out of solution on the protein, thereby reducing the amount of free glycogen in solution and causing the formation of more to re-establish the equilibrium. When we say that there is an equilibrium between glycogen and lactic acid we do not mean that the glycogen necessarily goes directly to lactic acid; on the contrary it probably goes through glucose or some hexose phosphoric ester and may even then go through some other intermediate stage such as methyl glyoxal before it finally reaches lactic acid.

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** Holder of Fellowship from the Cancer Research Laboratory of the Graduate School of Medicine of the University of Pennsylvania.

The early work of those interested in the changes in frog's muscles led to a mass of conflicting results, which was not cleared up until the classical work of Fletcher and Hopkins[1] in 1907. They say: "Abundant lactic acid formation is said to accompany the process of natural rigor in a surviving muscle (duBois-Reymond, Ranke, Boehm, Osborne), but this is denied (Blome, Heffter); it is said to accompany contraction, and to mark the advance of fatigue (Heidenheim, Ranke, Werther, Marcuse), but this is also denied (Astachewsky, Warren, Monari, Heffter). Indeed it may be said that since Ranke wrote in 1865, no description of the elementary facts of lactic acid formation, despite the fundamental importance of the subject, has been generally accepted."

Fletcher and Hopkins point out that most of the fallacies are due to faulty methods of extraction of the muscle in order to determine the lactic acid content. Thus, many workers procured values for the lactic acid of the resting muscle as high as that of the fatigued, and so believed that there was no change. Also troubles due to bacterial infection were prevalent.

Fletcher and Hopkins studied the formation of lactic acid under various conditions. Using induced interrupted current from two Daniell cells with a secondary coil (0.5 cm.) they found a maximum production of lactic acid which lay between 0.18 and 0.25% with a high value of 0.28% and an average value of 0.21%. These values also confirm the value of 0.229% found by Marcuse.[2] Meyerhof, as we shall see, got somewhat higher values than this with slightly less cumbersome methods of analysis.

The effect of chemical reagents is to form lactic acid very rapidly. At 20°C four hours exposure to chloroform vapor gives a yield of lactic acid of 0.434% whereas the control showed 0.02%. Similarly a like amount of lactic acid may be produced by heat rigor in the same time. This is accomplished by heating the muscle at 40°C and a maximum of about 0.42% was formed. "We find that an acid maximum is reached on heat rigor effected at or near 40° and this maximum is approximately on the same level with that produced in chloroform rigor, or in the slow death by alcohol." The alcohol in four hours gives values slightly over 0.40%.

Lactic acid may be formed in another way—by anaerobic rest. The rate of formation in this case is very much slower than by fatigue or by chemical means. In the course of 20-25 hours a maximum is reached which amounts to about 0.36% at 20°C. This is slightly higher than found for the frogs stimulated for a much shorter period (2 hours) and it is less than the maximum reached by chemical means in four hours.

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[1] J. Physiol., **35**, 247 (1907).

[2] Pflügers Archiv, **39**, 425 (1886).

In 1919-1920 Otto Meyerhof published a series of papers[1] on this subject. He fatigues muscles in two ways, namely, by tetanic stimulation and by induction shocks. The results from these two methods were not the same, for he found with single induction shocks values 40-60% higher than by tetanic stimulation. Meyerhof calls attention to the fact that, by using different methods of extraction from Fletcher and thereby shortening the time of manipulation, he obtained analogous maxima but in each case 15 to 20% higher. For tetanic stimulation Meyerhof finds a net increase of 0.205%, occasionally dropping to a value of 0.178% as in December, and with a high value of 0.24%. His values for single induction shocks are about 0.35%, dropping in December to 0.254%. In each case, however, the corresponding values are 40 to 60% higher for the single induction shocks than for tetanic stimulation. Incidentally these values are not affected by the means of inducing the stimulation—namely, whether applied indirectly to the nerves or directly to the muscle.

The rate of formation of lactic acid was studied with respect to single induction shocks and is of interest. Meyerhof carried on a series of experiments with incomplete fatiguing and compared the fatigue maximum reached under similar conditions (frogs from the same source, same time of year, temperature, and method of stimulation). He found in one experiment with indirect stimulation in 20 seconds (spark gap 15-17 cm.) a lactic acid content of 0.139%; in another stimulated for 40 seconds and another for 20 seconds he found 0.13% lactic acid. By using exhaustive tetanic stimulation a fatigue maximum of 0.23% was obtained and in less than one minute over half of the lactic acid was formed.

Metronome stimulation. By exhausting stimulation of fresh fall frogs—0.36%

2 minutes	0.118 %
6 "	0.168%
7 "	0.226%

We can see that 0.118% or a good half of the lactic acid was formed in the first third of the time.

Meyerhof gets results for chemical rigor similar to those Fletcher and Hopkins did, although his are slightly higher. He gets values ranging from 0.42% in the spring to 0.552% in the fall. These values are considerably higher than those found for electrical stimulation at the same times of year. The question naturally comes up as to why these values are higher and also why the chloroform causes the formation of lactic acid anyway. This last question is explained by Meyerhof by assuming that the chloroform in some unknown way causes a stimulation in the muscle which is more vigorous than the electrical stimulation and hence causes the formation of more lactic acid. Heat rigor has a similar action to chloroform and Meyerhof finds practically the same values for this as for chloroform.. This is in confirmation of the similar results found by Fletcher and Hopkins. Lacquer[2] has shown that, if two percent bicarbonate solution is added to cut-up muscle, a formation of lactic acid takes place which amounts to 0.9% as opposed to 0.4% in the ordinary salt solution. From this he ascribes the increasing acidity as the method which stops the acid formation. This is undoubtedly one of the factors and it is interesting to note, that neutralization of the acid should increase the yield if the reaction were an enzyme as we postulate, for we are taking away one of the final products.

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[1] Meyerhof: Pflugers Archiv, **182**, 232, 284; **185**, 11 (1920); **188**, 115 (1921).

[2] Lacquer: Z. physiol. Chem., **93**, 60 (1914).

Meyerhof also conducted some experiments on the formation of lactic acid during anaerobic rest; but his values are not easily comparable with those previously given here, because he added $NaHCO_3$ and HCN to his solution. As we have seen, the bicarbonate increases materially the yield of the lactic acid and Meyerhof himself seems doubtful whether the HCN does not also have an effect. However, he did find that the acid accumulation was slow and, even with the bicarbonate neutralizing some of the acid formed, he found an end value of 0.56% whereas Lacquer found a value for heat rigor and bicarbonate of 0.9%. So we see that this value is considerably less than the value procured for heat rigor and this was shown to be the case by Fletcher and Hopkins without the addition of bicarbonate.

In any study of the muscle or analysis of the results there are several factors which must be kept in mind in order to get a true insight into the working on the muscle. The first of these is the effect of the time of year. Fletcher and Hopkins (loc. cit., p. 226) say, "The infliction of heat rigor is a convenient method for determining the potentiality of a muscle for acid production at any time. Selecting observations made in other connections and at different times of year, we find that they fall into two groups according to season, thus giving only one for each six months,

March	383		October	.54	
April	.315		November	51	
May	420	Av. 36	December	.52	Av. .52

Whilst we have always found a surprising constancy in the value for the acidity of heat rigor, when duplicate determinations have been made on frogs caught under similar conditions, we have constantly found higher acid maximum for the muscles of autumn frogs than for those of frogs caught in the spring."

Meyerhof also finds differences at different times of year for rigor, chloroform, and the two stimulation maximums. The simplest explanation would seem to be that the glycogen content is different in the different months and indeed it has been shown by Mitchell[1] that oysters at different times of year have markedly different glycogen content. This explanation would be perfectly satisfactory from the point of view of our enzyme theory of equilibrium; but it does not seem to satisfy Meyerhof and his beliefs of the metabolic changes in muscles.

He says:[2] "What causes the difference in the lactic acid maxima in the different months? From the experiments of Lacquer on the regulation of the lactic acid maximum by H ion, we must conclude that there is a changing sensitiveness in the different months rather than a change in the glycogen supply. This is perfectly plausible. One finds that the anaerobic exhaustion through electrical stimulation is restricted by the addition of acid." Moreover he points out that the rigor maximum is smaller in the winter after the frogs have lain dormant for several months than in the fall. This would seem quite natural as the glycogen content should be lower. It is plain that Meyerhof is trying to explain two different factors by one explanation. These two factors are made clear on the basis of the enzyme theory of lactic acid production, for one would expect less lactic acid to be formed in the spring if there was less glycogen present, even as in the fall one would expect more lactic acid to be produced if there was more glycogen present. In any equilibrium if the final product is taken out, more of this product will be formed in order to reestablish the equilibrium. The action of the carbonate is to extract some of the lactic acid by neutralization and hence cause more to be formed. This last has no effect however on the changes of the amount of lactic acid formed due to the time of year.

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[1] Mitchell: U. S. Bureau of Fisheries, **35**, 151 (1916).

[2] Meyerhof: Pflügers Archiv., **182**, 232 (1920).

Another factor which must be taken into consideration is the effect of temperature. Meyerhof found that variations due to temperature affected the maxima formed by all the methods of producing lactic acid. At 0°C the maximum reached by stimulation was singularly small. The difference in the maximum caused by changes from 14° to 22° is much less than from 0° and 20° but the change is still considerable, for Meyerhof found an average value at 14° of 0.17% and at 22° an average value of 0.21%. The muscle apparently becomes fatigued much more rapidly at the lower temperatures, for he found that a muscle fatigued at 5°C was again irritable if heated up to 20°C. This is entirely in keeping with the findings that the muscle will produce more lactic acid at the higher temperature. There is a limit, however, for Fletcher and Hopkins have shown that in boiling water the muscle will not form lactic acid. This is due to the fact that the enzyme has been destroyed.

Cavallo and Weirs[1] showed that a muscle exhausted at 0°C if heated up to 25° and then cooled down again was able to have a new series of contractions. They believed that the process of heating up and cooling down made the muscle irritable again. Meyerhof was unable to verify this result and he points out that, if one waits long enough after the subsequent cooling down in order to insure that the entire muscle is again at the lower temperature, and if one takes precautions to provide anaerobic conditions throughout the manipulation, the muscle after cooling is still unirritable. It is not the change in temperature itself which causes the change in irritability but the fact that at the higher temperature the muscle can produce more lactic acid than at the lower temperature.

We have seen that it is possible to produce lactic acid in the muscle by several different methods. The question immediately arises as to where the lactic acid comes from. Meyerhof has demonstrated conclusively that, as the lactic acid increases, the carbohydrate decreases in exactly equivalent amounts. This change moreover, concerns chiefly the glycogen as the amount of change of other carbohydrates is small in comparison. He has shown[1] that during anaerobic rest the carbohydrate decreases as the lactic acid increases.

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[1] Cavallo and Weirs: J. Physiol. Pathol., 1, 990 (1899).

	Mg. Glucose		Mg. Glucose per gram Muscle		
	Before	After	Before	After	Difference
Muscle Wt., grams	10.2	10.35			
Glycogen	77.	45.2	7.55	4.35	−3.20
Other Carbohydrates	19.0	15.5	1.85	1.50	−0.35
					−3.55
			Corrected		−3.75
Lactic Acid			0.20	2.82	+2.62

In conjunction with the foregoing experiment Meyerhof also determined the resting respiration and he was then able to calculate the amount of carbohydrate burned by this respiration. This amounted to 1.1 mg. If we subtract this value from the amount of carbohydrate decomposed, we have the amount of lactic acid formed. Taking the value 3.75 mg. from the table and subtracting 1.1 mg, the amount burned, we have 2.65 mg. which should be converted into lactic acid. This checks very well with the value 2.62 mg. of lactic acid determined. So we see that, as the carbohydrate decreases, the lactic acid increases in exactly equivalent amounts.

The foregoing relation was found in whole muscle and in the following we find the same result in minced muscle in phosphate solution.

Time	Lactic acid Increase mg./gr.	Glycogen Decrease mg./gr.
8h. I	+ 0.272	−0.285
2h. II	+ 0.30	−0.34
23h. III	+ 1.056	−1.00
7h IV	+ 0.885	−0.895

The formation of lactic acid from glucose by enzyme action is not a new theory. In attempting to find out what the intermediate products in the decomposition of glucose to lactic acid were, Embden and his co-workers[2] carried out some liver perfusion experiments with glyceric aldehyde and dihydroxy-acetone. They showed that both substances increased the lactic acid in the perfused blood but that the glyceric aldehyde was much more effective. Embden advanced the theory that optically active glyceric aldehyde is the intermediary substance formed in the break-down of glucose into d-lactic acid. Neuberg and Rosenthal[3] found that fresh liver tissue would split methyl glyoxal into a mixture of dl and d-lactic acids. Whether methyl glyoxal or glyceric aldehyde or dihydroxy-acetone is the intermediate product between glucose and lactic acid is outside the scope of this work. The important point is that these authors realize the necessity of the presence of an enzyme in order to get optically-active lactic acid. Dakin and Dudley[1] added a solution of phenyl glyoxal to minced tissue and found a 40% to 60% conversion into l-mandelic acid. They found that increasing acidity stopped the conversion completely and that, to get this conversion, it was necessary to add sodium bicarbonate to keep the H ion down. Moreover, the enzyme present here was killed if the tissue was boiled, which is just what would be expected. They also found that an enzyme solution prepared from dog's liver decomposed 4 grams of pure methyl glyoxal into lactic acid completely in 10 minutes. They were unable, however, to get only d-lactic acid but got a mixture. Levene and Meyer[2] showed that leucocytes and kidney tissue formed lactic acid from methyl glyoxal under aseptic conditions and that a mixture of the dl and d-forms were obtained. They also showed[3] that these leucocytes could change glucose into optically active lactic acid. From this they concluded that glucose must break down into lactic acid by way of methyl glyoxal.

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[1] Meyerhof: Pflugers Archiv, **185**, 11 (1920).

[2] Biochem. Z., **45**, 108 (1912).

[3] Neuberg and Rosenthal: Biochem. Z., **49**, 502 (1913).

Meyerhof refers to these authors in a monograph "Chemical Dynamics of Life Phenomena," 59 (1924) by saying: "They seem to assume that a reversible equilibrium exists between sugar and lactic acid, so that the reaction could go spontaneously either in one or the other direction. This is however, not the case, as will be shown in detail later. The cleavage of sugar into lactic acid is a spontaneous process going to completion. On the other hand the synthesis of sugar from lactic acid requires a supply of energy furnished in the isolated muscle exclusively by oxidation of part of the lactic acid or the corresponding amount of sugar. It can probably be provided also in the other organs only by oxidation."

As we have seen, the methyl glyoxal apparently breaks down completely into lactic acid, yet Dakin has shown conclusively that the equilibrium between methyl glyoxal and lactic acid is reversible.[4] An aqueous solution of lactic acid and the enzyme was digested at 37°C. Upon addition of nitrophenyl hydrazine a precipitate of the insoluble methyl glyoxal dinitro phenyl hydrazone was formed, which could be readily separated and analyzed. The fact that the glycogen breaks down completely into lactic acid under certain conditions does not necessarily mean that there can not be an enzyme equilibrium. The conditions necessary to cause all the glycogen to break down is a considerable excess of phosphate which might have the effect of neutralizing the lactic acid formed, thereby displacing the apparent equilibrium.

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[1] Dakin and Dudley: J. Biol. Chem., **14**, 155 (1913).

[2] Levene and Meyer: J. Biol. Chem., **14**, 551 (1913).

[3] Levene and Meyer: J. Biol. Chem., **12**, 265 (1913).

[4] Dakin: J. Biol. Chem., **14**, 555 (1913).

Meyerhof has shown that in phosphate solution all the glycogen is decomposed; but that does not mean that all the carbohydrate has decomposed as one is led to believe. Two of his experiments on this might well be quoted here.

G = Glycogen
K = other carbohydrate

Time from start of mincing	Carbohydrate Content Total mg.	Carbohydrate Content %	Lactic Acid Total mg.	Lactic Acid %
20	G = 31.4	0.898	2.23	0.064
	K = 9.5	0.27		
August 23h	G = 0	0		
	K = 8.6	0.25	39.2	1.12
Total		−1.00		+1.056 corr.
15	G = 12.4	0.214	4.05	0.010
	K = 13.5	0.231		
8h 15	G = 0	0.0		
	K = 10.5	0.180	20.0	0.342
Total		−0.285		+0.272

We see from these figures that all the carbohydrate has not disappeared, even though all the glycogen has. The argument that Meyerhof puts forth, that there can be no enzyme reaction because all the glycogen disappears, is not sound. In the first place he may have been neutralizing the final product with the excess of phosphate which would displace the apparent equilibrium. Dakin showed that methyl glyoxal apparently went completely to lactic acid but he was able to show conclusively that the equilibrium was reversible.

Meyerhof has suggested that in all probability glycogen breaks down into lactic acid perhaps through glucose and probably through an intermediate hexose phosphoric ester. Lacquer[1] has found that glycogen is a better source of lactic acid than glucose in the separated muscle. According to him the reason for this seems to be that only *α* glucose which is a derivative of glycogen yields lactic acid immediately whereas *β* glucose must first change into the *α* form.

As we have pointed out before, we assume that the formation of lactic acid is due to an equilibrium between glycogen and lactic acid, whose rate is governed by enzymes. In the decomposition of glycogen there may be an intermediate formation of *α* glucose and probably a hexose phosphoric ester and perhaps some further intermediate compound as methyl glyoxal before the lactic acid is reached. Furthermore the equilibrium point is well over on the lactic acid side.

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[1] Lacquer: Z. physiol. Chem., **116**, 169 (1921).

Glycogen
$(C_6H_{10}O_5)_n$
⇅
Glucose or Hexose phosphoric ester or both
$C_6H_{12}O_6$
⇅
Methyl Glyoxal
CH_3COCHO
⇅
Lactic Acid
$CH_3CHOHCOOH$

These might possibly be the steps in the reaction. No attempt is made in this paper to determine the steps; but it is helpful to have a picture of what may happen in a simplified form in order to understand the processes.

Przylecki and Wojcik[1] have shown that protein has an extraordinarily high adsorptive power for glycogen, and that, using appropriate concentrations of the protein, which incidentally correspond to those present in the liver, this adsorption may even for 10% glycogen solutions, amount to as much as 90%. With 30 cc. of a 1% glycogen solution and 30 grams of protein, 99% of the glycogen is adsorbed out of the solution. This adsorption of glycogen is a reversible reaction, for they have shown that by diluting with a sufficient quantity of water the glycogen may be eluted off the protein again. It may be liberated also by the action of various chemicals such as alcohol, and other narcotics. Przylecki worked principally with the enzyme amylase which hydrolyzes glycogen to glucose; he showed that, when the glycogen was adsorbed on the protein, it was so stabilized that the rate of reaction with the enzyme was very slow but in the course of time it was broken down into glucose. If in the muscle the enzyme only reacted with the free glycogen, we should expect during anaerobic rest that the formation of lactic acid would be slow, as the concentration of free glycogen in solution at any time would be small. As the concentration of free glycogen diminished, glycogen adsorbed on the protein would be set free to reestablish that equilibrium, and the free glycogen thus formed would in turn be decomposed to lactic acid until perhaps the increase in hydrogen ions stopped the process.

Fletcher and Hopkins,[2] in order to account for the linear formation of lactic acid, suggested such a possibility as this equilibrium between adsorbed glycogen and free glycogen. They say: "Conceivably the store of precursor in the muscle is partly in insoluble form, partly in solution, the concentration might be kept constant by replacement from the insoluble store, and, for a period, conditions would exist for a linear rate of change. The explanation is probably less simple than this, and it is interesting in any case, to observe how in the quiescent unstimulated muscle the survival processes which lead to lactic acid production are so controlled as to lose the exponential character of an isolated chemical reaction."

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[1] Biochem. J., **22**, 1302 (1908).

[2] Loc. cit., p. 275.

In the case of electrical stimulation we have seen that more lactic acid is formed by single induction shocks than by tetanic stimulation. Meyerhof says: "How can one explain that by single induction shocks which are applied sixty times to the minute a much greater amount of lactic acid accumulates in the same time than when twenty-five times the number of irritations were applied tetanically." He points out that by the use of a tension lever it can be shown that the muscle irritated by single induction shocks performs more work than those stimulated by tetanus. Moreover a muscle which has been exhausted by tetanic fatigue is still irritable to single induction shocks. The lactic acid, according to Meyerhof is a measure of the work done; and since more work was done in the stimulation by the single shocks more lactic acid should be formed. This is, of course, arguing in a circle. We have seen that the glycogen is stabilized by adsorption on the protein, and stimulation causes the glycogen to be liberated from its adsorption thereby increasing the concentration in free solution. As the concentration increases in free solution the rate of formation of lactic acid increases. Indeed, we have seen that where 0.22% was formed in seven minutes, over half was formed in the first two minutes when the concentration was the highest. Just how the contraction of the muscle causes the liberation of the glycogen is, at this time, pure conjecture. Bancroft and Richter[1] have shown that a man rendered unconscious by an electric shock is in reality in a state of narcosis. Now in narcosis, as they have demonstrated, the proteins are reversibly coagulated, that is if the cause of the coagulation is removed the proteins will return to their peptized state again. In the case where proteins are irreversibly coagulated the patient dies. Probably the contraction of the muscle coagulates the protein slightly, causing a liberation of some of the adsorbed glycogen. However, this coagulation is not due to the effect of the electrical current itself, for Meyerhof has shown that it makes no difference whether the current is passed directly to the muscle or directly through the nerves. The coagulation due to a single twitch is probably slight with a correspondingly small liberation of glycogen. With a single tetanic stimulation the muscle is tetanized, or fully contracted, so that continuous stimulation would have little further effect on the muscle. If a very short period of rest is allowed between tetanic stimulations, the muscle would tend to relax, thus allowing further stimulation to contract it again. It is for this reason essential to allow short periods of rest in tetanic stimulation in order to procure the maximum yield of lactic acid. These periods of rest are only momentary, as the tetanic stimulations are applied well over sixty times to the minute. We know from

[1] Bancroft and Richter: J. Phys. Chem., 35, 215 (1931).

Meyerhof's work that a muscle is still irritable to single induction shocks even though fatigued to tetanic stimulation, so that there are more contractions with the former method, more glycogen liberated, and hence, just as we should expect, more lactic acid formed. In this particular case, Meyerhof's explanation of lactic acid as due to the work done by the muscle is nearly as satisfactory as our explanation.

In the case of the quiescent unstimulated muscle under anaerobic conditions we should expect to get a slow formation of lactic acid, as the glycogen in free solution would be decomposed to glucose and hence to lactic acid. As the free glycogen diminishes, more glycogen would be liberated from the protein to keep the concentration constant. As the concentration of free glycogen is small at any particular time, we should only expect a slow rate of reaction. Meyerhof's explanation of work done could not hold in this case as no work is done by the muscle in this quiescent state. We can predict what should happen in this case, but do the facts support this prediction? We have seen that a maximum yield of lactic acid in this case is not reached in a few minutes as is the case when the muscle is stimulated electrically but in the course of 23 hours. Moreover, according to Fletcher and Hopkins the rate of formation follows a linear course, which is what we should expect from the fact that the concentration of free glycogen is constant.

We do not need to postulate, as Meyerhof does, that the addition of chloroform in some unknown way causes a stimulation of the muscle and in that way produces lactic acid. We have only to bear in mind the fact that the chloroform coagulates the protein thereby liberating the adsorbed glycogen. The increase of the concentration of the free glycogen would increase the rate of formation of lactic acid. Indeed we find that the addition of chloroform causes a formation of lactic acid which reaches a maximum in four hours or less. The effect of the addition of chemical reagents probably liberates more glycogen than stimulation methods do so that there is more lactic acid formed. Heat rigor may be explained on the same basis, as it is well known that heat will coagulate the proteins. Ether and alcohol apparently have the same effect as chloroform and come under the general head of narcotics. Some other chemicals as arsenate and caffein have slightly different effects. Bancroft and Richter (loc. cit.) have shown that caffein in high enough concentrations acts like a narcotic in coagulating the proteins. According to Przylecki the explanation of the increased formation of lactic acid may not be as simple as this. They say:[1] "The acceleration of the velocity of hydrolysis caused by the addition of narcotics, such as chloroform, ether, or alcohol might on the basis of this research be explained as being due exclusively to elution of polysaccharide. While such an explanation appears to fit very well with experimental findings, it should not be forgotten that in our case we are dealing with a system simpler than that present in our cell, as it contains only one of the components of the latter, namely protein. The possibility remains that, within the cell, enzyme is adsorbed not only on its protein elements, but also upon lipin or nucleoprotein surfaces, from which elution by narcotics may be much greater than from proteins."

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[1] Przylecki: Biochem. J., **22**, 34 (1928).

"There can be no doubt that elution of substrate from protein, or change in the state of dispersion of the latter, plays an important part in the acceleration of the velocity of enzyme by hydrolysis of polysaccharides due to the addition of narcotics."

It has been assumed, and qualitatively at any rate the facts seem to bear this out, that the enzyme only affects the free glycogen and not the adsorbed glycogen. However, if there is a combination of enzyme and substrate in the reaction which the enzyme catalyzes, there might also be a combination with some of the adsorbed glycogen. The facts seem to support the belief that the enzyme combines only with the free glycogen, as we have seen in the case of anaerobic rest. Nevertheless this is not the whole story, for the problem might be further complicated by adsorption of part or all of the enzyme under certain conditions. Thus, with the enzyme 100% adsorbed on the lipin surfaces and the glycogen 100% adsorbed on the protein, there would be no reaction. If both are only partly adsorbed the effect of some chemicals might be to liberate only the enzyme, or only the glycogen, or both at once and in each case the resulting effect would be different. There does not seem to be any need in making the problem as complicated as this, for there does not seem to be any evidence as yet that requires us to assume that the enzyme combines with the adsorbed glycogen. On the other hand the enzyme is undoubtedly adsorbed to some extent on the lipin surfaces; but Przylecki has shown that this does not necessarily impair its action on the free glycogen. As Richter and Bancroft have shown, the effect of chemical reagents may be of another class, those which do not coagulate the protein but which are selectively adsorbed on it. These substances, depending on their concentration and the degree of adsorption, would have different influences on the formation of lactic acid. Furthermore substances which would tend to increase the peptization of the protein might increase the degree of adsorption and thereby decrease the tendency towards lactic acid formation.

Another essential, but hitherto unconsidered point, is the question why the lactic acid formed in the muscle is dextrorotatory. Evans[1] has shown that glucose under the influence of strong alkali yields lactic acid, but the product is inactive. This might be due to racemization of the acid by the strong alkali; but this is improbable, as dilute alkali also yields inactive lactic acid. Moreover, if the glucose passed through an intermediate stage of methyl glyoxal or pyruvic acid, both of which are inactive, the final product would be inactive unless an enzyme were present. It has been pointed out earlier in this paper that, methyl glyoxal in the presence of an enzyme known as glyoxalase yields active lactic acid, and leucocytes and kidney tissue can decompose glucose into optically active lactic acid indicating the presence of an enzyme. Indeed Meyerhof[1] has shown that an enzyme can be extracted from muscles which upon purification is many times more active than the muscle itself, and that this enzyme can convert glucose and glycogen into lactic acid. Presumably this is optically active lactic acid although he does not say definitely.

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[1] Evans: J. Am. Chem. Soc., **47**, 3085 (1925).

Meyerhof has pointed out that the formation of lactic acid is due to several causes, among which the respiration plays an important part in determining the rate. If however, the formation of lactic acid is due, as we believe to enzyme action, increase of the starting products should increase the rate of formation of lactic acid. Stiven[2] has shown that increasing the concentration of glycogen with the enzyme extracted from cat's muscle, increases the rate of formation of lactic acid. The following diagram shows this increase.

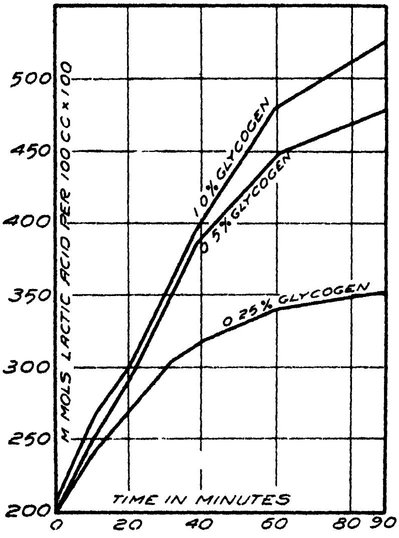

Fig. 1
From Biochem. J., 22, 872 (1928)

We see from this diagram that as the concentration of glycogen increases the rate of formation of lactic acid increases. This is exactly what we should expect from an enzyme reaction. The concentration of the enzyme was constant in the three cases.

What is the fate of the lactic acid during the recovery period in oxygen? So far, we have only considered the anaerobic or working phase. Fletcher and Hopkins found that, with a separated muscle after repeated stimulation and recoveries in oxygen over a period of several days, the yield of lactic acid from heat rigor was practically the same as for fresh muscle. It has been known for some time that a muscle which has been fatigued and then allowed to rest in oxygen recovered its irritability again. In other words the lactic acid, which is a measure of the fatigue, had disappeared. From their experiment Fletcher and Hopkins assume that the lactic acid, all or in part, must be converted back into carbohydrate again in oxygen, for if it was all burned the amount of lactic acid from heat rigor after several days of repeated stimulations and recoveries would be materially reduced.

Hill[3] found that in the oxidative removal of one gram of lactic acid there is a heat production of about 450 calories. Now the oxidation of one gram of lactic acid leads to a heat production of about 3700 calories, which is about eight times as large as the quantity observed. Although the measurements were not very accurate it is obvious that all the lactic acid is not burned, but that some is returned to its precursor, glycogen, under the influence and with the energy of the oxidation, either (a) of a small part of the lactic acid itself, or (b) some other body.

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[1] Meyerhof: Naturwissenschaften, 14, 196, 756, 1175 (1926); Biochem. Z., 178, 395, 462 (1926).

[2] Stiven: Biochem. J., 22, 867 (1928).

[3] Hill: J. Physiol., 48, x (1914).

In 1922[1] a more careful study of the liberation of heat showed that there are three stages in which heat is given off in the working muscle, which Hill characterizes as the initial anaerobic heat, the delayed anaerobic heat, and the oxidative heat. These amount to 285, 85 and 340 calories respectively. If we suppose that of one gram of lactic acid x grams are oxidized in the recovery and $(1 - x)$ grams restored to its previous state as glycogen, the muscle will have returned to normal except for the x grams oxidized. The heat of combustion of glycogen according to Stohmann is 4191 cal./gr. and according to Emery and Benedict 4227 cal/g. If we take the mean of these two quantities, namely cal./g., we see that the heat of combustion of 0.9 g. of glycogen which corresponds to 1 gram of lactic acid is 3788 calories. Hence the total energy available to cover all breakdowns in the complete cycle is 3788 × cal. Equating this to $(285 + 85 + 340 = 710$ cal.,), we find $x = 710/3788$ or 0.188. Thus of one gram of lactic acid passing through the whole cycle of contraction and recovery 0.188 gr. are oxidized and the remainder viz. 0.812 grams are restored to its previous state as glycogen. We can see, therefore, that one-fifth to one-sixth of the lactic acid is burned and the remainder is converted back into glycogen.

These myothermic measurements of Hill's do not show what the lactic acid is converted into, as there was no chemical analysis of the changes. Meyerhof[2] however, in a study of the carbohydrate exchange of frog's muscles demonstrated that, as the lactic acid disappears during the recovery period, so the carbohydrate increases in exactly the extent as calculated from the difference of the lactic acid disappearance and the oxygen consumption (recovery consumption minus resting consumption). Again the change concerns the glycogen chiefly, and there is a synthesis of glycogen from lactic acid. The glycogen content at the end of the recovery period is the same as before the stimulation, minus the carbohydrate disappearance equivalent to the oxygen consumption. To quote one experiment of Meyerhof's where he found the following balance in mg./g. of muscle.

	Before recovery	After recovery	Difference
Glycogen	3·37	4·75	+1·38
Other Carbohydrate	2.01	1.66	−0·35
	5·38	6.41	+1.03
Lactic acid	2.56	0·44	−2.12

In oxygen experiments carried on at the same time, he found 1.20 mg of excess oxygen were used in the recovery period which would burn 1.12 mg. of lactic acid, so we see that 2.12 − 1.12 or 1.00 mg of lactic acid should have been converted back into glycogen. This checks very reasonably with the determination that 1.03 mg of glycogen were formed.

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[1] Hill: J. Physiol., **56**, 367 (1922).

[2] Meyerhof: Pflügers Archiv, **182**, 284 (1920).

Meyerhof has also shown that, if the muscles are not minced too finely, there is apparently a formation of glycogen in the aerobic phase which indicates that there is no necessary relation between structure of the muscle and the formation of glycogen. When the muscle is minced very finely, the negative results are probably due to a diffusion of phosphate away from the enzyme, thus preventing the esterification of the glucose to the intermediate glucose phosphoric ester. This is in accord with his findings for the necessity of phosphate for the decomposition of glycogen to lactic acid.

Let us now consider Meyerhof's explanation for the recovery period in the muscle. In "Chemical Dynamics of Life Phenomena," 55 (1924), he says: "In the oxidative phase one molecule of sugar or the corresponding amount of lactic acid is burned. The rest of the lactic acid is reconverted with phosphate to the ester (glucose phosphoric ester) and again becomes glycogen. Here we have a coupled reaction similar to the alcoholic fermentation."

In short he assumes that the oxidation and synthesis is a coupled reaction, where the synthesis cannot take place without the oxidation to supply the energy for it. From a purely chemical point this reaction should not require much energy, as glucose stoichiometrically is exactly two molecules of lactic acid, and glycogen is a straight polymer of glucose with a splitting out of water. If this is in reality a coupled reaction, one should be able to take lactic acid, oxidize it in the presence of protein, and form glycogen. It apparently does not require the muscular structure as Meyerhof found a synthesis of glycogen with minced muscle. Lactic acid is oxidized readily in the presence of ferrous salts by hydrogen peroxide but there is no formation of glycogen under these conditions even in the presence of protein which would naturally adsorb any glycogen that was formed. Indeed from our hypothesis of an equilibrium between glycogen and lactic acid, catalyzed by enzymes, we should not expect to form any glycogen under these conditions.

It is our belief that the oxidation of lactic acid is not coupled with the synthesis of glycogen, but occurs simultaneously in the presence of oxygen. We have stated that we assume that glycogen and lactic acid are in equilibrium, the reaction being catalyzed by enzymes. When the muscle is stimulated, considerable quantities of glycogen relatively are liberated from adsorption on the protein, and this free glycogen changes over to lactic acid due to the fact that the equilibrium point between glycogen and lactic acid is well over on the lactic acid side. When the muscle comes to rest, on the other hand, in the presence of oxygen, the concentration of adsorbed glycogen has been considerably reduced from what it was before the stimulation. To re-establish this former state more glycogen must be adsorbed out of solution. We know from the mass law that, when two substances are in equilibrium, extraction of one substance will cause a formation of that substance from the other in order to re-establish the equilibrium. In other words, as the glycogen is taken out of solution by the protein, more glycogen will be formed from lactic acid in order to keep the equilibrium constant. In this way three quarters of the lactic acid which disappears is reconverted into glycogen. The other one quarter is burned by the oxidation which occurs at the same time. It is not necessary that there should be a great amount of synthesis at any one time for, as glycogen appears, it is extracted from solution by adsorption until the amount of adsorbed glycogen has reached the normal resting value. Bayliss in "The Nature of Enzyme Action," 56 (1925) says: "It might be thought that a synthesis of a small degree could not be of much practical importance. This would be an error, as the following considerations will show. Let us take the case of amylase where the hydrolysis progresses almost to completion, and let us suppose that no more than one percent of starch is formed when the enzyme acts as maltose or dextrin. Since the product is an insoluble body, the equilibrium will exist only for a moment, so that more starch will be formed in order to replace that thrown out of the system by precipitation. As the rate of this reaction is slow, as shown above, the amount of starch per unit time will not be great, although by no means negligible. The process, it will be noted, is analgous to that of the precipitation of chloride as silver salt. It is most likely as Croft Hill[1] points out, that the storage of starch in the plant and that of glycogen in the animal are to be explained on these lines."

In such an enzyme equilibrium where the glycogen is adsorbed out of solution on the protein, thereby displacing the equilibrium and causing the formation of more glycogen, the rate of recovery to the normal state must necessarily be slow, as there is only a small amount of synthesis at any one time. Meyerhof has shown that the recovery period is slow, requiring fifteen to twenty-three hours before the muscle returns to its normal resting state. This could be prophesied from our theory but would not necessarily be so if the synthesis were coupled with the oxidation of lactic acid.

If the glycogen and lactic acid are in an equilibrium whose rate is catalyzed by enzymes, we should expect, all other things being equal, that increase in the amount of glycogen should increase the rate of reaction and the amount of the final product lactic acid. Thus ten milligrams of glycogen with the enzyme should be converted to lactic acid more rapidly than one milligram and with a larger final yield of lactic acid. This was apparently the case in the experiments of Stiven which have been cited. It should be borne in mind, however, what is meant by all other things being equal. The enzyme concentration must be constant throughout the reaction. Moreover the final products must not affect or poison the enzyme. Dakin found that the enzymic conversion of phenyl glyoxal to l-mandelic acid was stopped completely by increasing acidity. In other words, the acid poisoned the enzyme. We know that the addition of bicarbonate increases very materially the lactic acid production in the muscle. This, however, may be a combination of two factors: one, reduction of the acidity; and two, extraction of the final product by neutralization. It is possible therefore, that, in any particular case, the increasing acidity might stop the reaction at a definite value of lactic acid.

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[1] J. Chem. Soc., 73, 634 (1898); J. Physiol., 28, Proc. XXVI.

When the muscle is stimulated and then allowed to recover in the presence of oxygen, part of the lactic acid is burned and part is converted back into glycogen. This means that the store of glycogen is becoming less and less, providing there is no replenishment from outside. This replenishment probably comes in the normal animal from the glucose of the blood. There is no provision in Meyerhof's theory for the formation of glycogen from glucose except by the way of lactic acid which seems improbable. Mitchell[1] has shown that the glycogen content of oysters may be very materially increased by feeding the oysters glucose in the presence of air. It seems distinctly unlikely that this glucose is first broken down into lactic acid before being converted into glycogen. From our enzyme theory it would be perfectly possible for the glucose to go either directly or, after esterification with phosphate, to glycogen, for the two substances must be in equilibrium. The glycogen would be formed as fast as it was adsorbed out of solution by the protein, otherwise the equilibrium would be displaced.

The formation of glycogen from lactic acid, as we have pointed out, depends upon the extraction of glycogen from solution on the protein, thereby disturbing the equilibrium and causing the further formation of glycogen in order to re-establish it. Under these conditions it should be possible to add lactic acid to the enzyme in the presence of a suitable protein adsorbent and perhaps phosphate and form glycogen.

Przylecki (loc. cit.) has shown that glycogen is strongly adsorbed on such proteins as are present in liver, as well as on coagulated egg white. Using 15 cc. of a 0.2% solution of d-lactic acid, 10 cc. of $M/2$ KH_2PO_4, and 10 cc. of enzyme solution and approximately 30 grams of egg white we attempted to show the formation of glycogen. That we were not able to establish the formation positively may be due to the present methods of analysis of glycogen.

The enzyme solution was prepared according to the direction of Meyerhof[2] in which the rabbit was killed by a blow on the head, the hind legs rapidly skinned, the muscles cut out and placed in a glass evaporating dish surrounded by carbon dioxide snow. The muscles were then cut into thin slices and extracted with 50 cc. of isotonic KCl solution at 0°C. The muscle residue was separated from the solution by centrifuging. The clear solution resulting from this procedure after two hours digestion with 0.8% glycogen solution showed a strong qualitative test for lactic acid. The qualitative test was that recommended by Fletcher and Hopkins on the formation of a cherry red color with thiophene after oxidation with $CuSO_4$ and H_2SO_4. It is interesting to note that in the same period when egg-white was added to the mixture, there was only a faint test for lactic acid. This is entirely in accord with the findings of Przylecki who showed that glycogen was hydrolyzed only very slowly by amylase in the presence of protein. Indeed it could have been prophesied from the theory that this would be the case when the glycogen was stabilized by adsorption on the protein.

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[1] Loc. cit.

[2] Naturwissenschaften, 14, 196, 756 (1926).

Evans[1] pointed out that all the glycogen is not precipitated when using Pflüger's method of analyzing for glycogen which necessitates the use of as much as 90 cc of solution in the precipitation of glycogen by alcohol after treatment with KOH. This will amount to a large percentage error when only small amounts of glycogen are present. In a very recent paper Kerly[2] says that this is probably due to the solubility of glycogen in aqueous alcohol, but there may also be some peptization by the KOH decomposition products of the protein. Holmes and Holmes[3] undertook some experiments to show that glycogen could be recovered from such a large volume of solution and they found that the glycogen could be recovered 100%. They, however, added solid glycogen to water and then precipitated it with alcohol, which according to Kerly does not resemble the true conditions, as she points out that 17 to 18 percent of the glycogen is in solution; but that it dissolves very slowly, taking a week to come to equilibrium. Under these conditions Holmes and Holmes were not precipitating glycogen from solution, and their good results may be attributed to this fact.

Inasmuch as we were working with egg albumin, enzyme, lactic acid, and perhaps glycogen, it seemed that the procedure might be simplified to precipitation of the protein, with a subsequent careful washing in order to remove all the glycogen. The protein was precipitated with mercuric chloride and with thorium nitrate in alkaline solution. Careful washing caused some of the protein to become peptized and pass over into the filtrate. If these last traces are not removed, reducing substances caused by the subsequent HCl hydrolysis affect the results materially, making them too high. The more serious difficulty, however, is that the last traces of glycogen cannot be removed from adsorption on the protein. Where small amounts of glycogen are present this amounts to a large percentage error, and makes the method impracticable for quantitative work.

This question of adsorption has not been considered carefully heretofore in the methods for determining glycogen. It is obvious that the usual means of testing the efficaciousness of a method by adding known amounts of glycogen to tissue already containing glycogen and showing that one can recover 100% of the added glycogen is no criterion for that method. There is the same error of loss due to adsorption both in the portion to which glycogen was added and also in the blank. This error is of course not so serious when one is merely comparing the relative amounts of glycogen in two samples, but it is necessarily of prime importance in our case where we have no glycogen in the blank and wish to show a formation of glycogen. We are now working on a method of analysis with which we hope to surmount these difficulties.

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[1] Biochem. J., **19**, 1115 (1925).

[2] Biochem. J., **24**, 67 (1930).

[3] Biochem. J., **20**, 1196 (1926).

It is interesting to note that one of the characteristics of cancer is a disruption of the ordinary metabolic changes in the muscle. The rate of formation of lactic acid is greatly increased and there seems to be little conversion of lactic acid back into glycogen. It is necessary for Meyerhof to postulate that the glycogen is broken down as fast as it is formed, for he claims that the glycogen is formed by the coupled reaction between oxidation and synthesis. This is absurd. Warburg and Negelein[1] have shown that the rate of formation of lactic acid in cancer is very little reduced by the presence of oxygen. On the other hand, in the normal tissue there is very little or no lactic acid formation in the presence of oxygen. This indicates that the formation of glycogen, which reduces the concentration of lactic acid, is reduced to a minimum in cancer tissue.

The increased rate of formation of lactic acid may be due either to an increased amount of available enzyme, or to less adsorption of glycogen on the protein. If some of the enzyme is ordinarily adsorbed on the lipin surfaces, as Przylecki suggests, this might be liberated by the selective adsorption of some foreign substance in cancer which would give an increased concentration of free enzyme. On the other hand, less adsorption of glycogen due either to less protein or to some substance being selectively adsorbed on it might account for the increased rate. With less adsorption of glycogen, according to our theory, there would be no reason for much formation of glycogen from lactic acid, and apparently there isn't. Due to the lack of facilities we have not been able to test whether there is less adsorption of glycogen by cancer tissue than by normal tissue.

Warburg also points out that carcinomas form lactic acid from methyl glyoxal at the same rate as from glucose, which is very surprising if methyl glyoxal is an intermediate compound between glucose and lactic acid. There should be a time factor unless the reaction between glucose and methyl glyoxal is instantaneous. Moreover he points out that liver tissue breaks down glucose at only one-tenth the rate of cancer tissue but breaks down methyl glyoxal at the same rate. He concludes from this that there is no difference between cancer and fresh tissue with respect to methyl glyoxal We conclude from this that either there is some mistake in the determination of the rates of lactic acid formation from glucose and methyl glyoxal, or, in carcinoma, glucose does not break down to lactic acid through the intermediate stage of methyl glyoxal. Warburg also calls attention to the similarity between embryonic and cancer tissue in the rapid growth, increased rate of glycolysis and the small amount of glycogen present.

This fact led Harrison and Mellanby[2] to the belief that the increased rate of glycolysis might be due to a lack of some substance 'the growth regulator' which was absent from the embryo and from the cancer tissue. Inasmuch as cancer seldom attacks the pancreas, they believed that this organ must contain considerable quantities of this hypothetical substance. They found that an extract of the pancreas did inhibit glycolysis in cancer tissue from 15 to 100 per cent both in the anaerobic and aerobic phase. They found, moreover, that cancer tissue could not form lactic acid from hexose monophosphate or diphosphate, whereas the normal tissue forms lactic acid from these substances readily. They came to the conclusion that in cancer tissue glucose does not go through the form of a phosphate ester before going to lactic acid, and that in this respect the cancer tissue was different from normal tissue. We know, however, that cancer forms lactic acid from glycogen rapidly. If Harrison and Mellanby are correct, this must mean that in cancer glycogen is not esterified with phosphate during the course of glycogenolysis. There seems to be ample evidence to show the formation of an intermediate phosphoric ester in the normal tissue. Furthermore we have seen from Warburg's work that glucose apparently breaks down into lactic acid without going through the stage of methyl glyoxal. On the basis of these facts we must conclude that glycogen and glucose are converted into lactic acid by different ways in cancer and in normal tissue. This difference in itself might possibly account for the difference in rate of glycolysis.

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[1] Warburg and Negelein: Biochem. Z., **152**, 309 (1924).

[2] Harrison and Mellanby: Biochem. J., **24**, 141 (1920).

The problem as outlined here of why and how glycogenolysis takes a different path in cancer than in normal tissue should be of considerable importance in the study of cancer. It is one of the problems which must be solved in the future.

The following general conclusions are made:

1. The theories of Meyerhof, Warburg, and Hill are not the only explanation for the chemical changes during fatigue and recovery in the muscle.

2. The amount and the rate of lactic acid formation may be readily explained on the assumption of an equilibrium between glycogen and lactic acid, whose rate is catalyzed by enzymes.

3. The slow linear formation of lactic acid during anaerobic rest is easily understood and could be predicted on the basis of an enzyme theory where the glycogen is stabilized by adsorption on the protein.

4. The formation of lactic acid as a result of chloroform and heat rigor is obvious when we realize that the effect of these agents is to liberate the glycogen from adsorption on the protein.

5. A suggestion has been made which should account for the effect of various other chemical reagents as caffein, arsenate, oxalate, etc.

6. An adequate explanation is put forward by means of this theory for the formation of dextrorotatory lactic acid in the muscle, a phenomenon which has been more or less ignored in the Meyerhof theory.

7. It has been shown that, despite the fact that the equilibrium point is well over on the lactic acid side, it is quite possible for the lactic acid to be converted back into glycogen again, due to the extraction of glycogen from solution by adsorption on the protein.

8. Some of the errors in the methods of analysis of glycogen have been pointed out which have prevented up to this time the demonstration of the formation of glycogen from lactic acid by means of the enzymes and the adsorption of the glycogen on the protein.

9. Glycogen apparently takes a different path in cancer in the formation of lactic acid from that which it takes in the normal muscle.

10. Several possibilities are suggested, any one or all of which might account for the increased rate of glycolysis in cancer.

We are indebted to Dr. Ellice McDonald of the Cancer Research Laboratories of the Graduate School of Medicine of the University of Pennsylvania who suggested this work and gave us valuable aid in supplying references.

Cornell University.

THE CHEMISTRY OF ANESTHESIA*

BY WILDER D. BANCROFT AND GEORGE H. RICHTER**

The working hypothesis of this paper is Claude Bernard's theory that the reversible coagulation of the colloids of the sensory nerves produces or accompanies anesthesia. This is supplemented by the plausible assumption that the decreasing stability of the colloids during the first addition of the anesthetic is accompanied by an increasing irritability.

Historical and mythological literature abound in fact and fancy concerning narcotics and their uses. Their use was sometimes attended with weird incantations, many strange concoctions, hypnotism, and always with a lack of scientific knowledge of the nature of the phenomena. That narcosis was well known at the beginning of the Christian era is established by the work of Galen and his contemporary, Dioscorides.[1] In spite of its antiquity, there is still considerable mystery surrounding the mechanism of narcosis. Modern textbooks on pharmacology are content to give several theories of narcosis and to point out good and bad features in each without definitely proving or disproving any particular one.

In 1899 Hans Meyer proposed a theory that was immediately followed by E. Overton's theory. Since the two theories were formulated separately and about the same time it is known as the Meyer and Overton theory. This is, perhaps, one of the most popular theories at the present time. It is based upon the fact that narcotics are soluble in lipoids or fats and that the strength of their action is related to the distribution coefficient. Meyer formulated the theory in the following way:

"(a) All chemically indifferent substances, which are solvents for fats and similar bodies, must exert a narcotic action upon living protoplasm, in so far as they can diffuse therein.

(b) The effect must manifest itself first, and most strongly, in those cells in whose chemical structures these fatty or lipoid substances predominate and presumably are the essential carriers of the cell function, namely, in the nerve cells.

(c) The relative efficiency of such narcotic agents must be dependent upon their mechanical affinity for lipoid substances, on the one hand, and for the remaining body constituents, i.e., principally water, on the other hand. It is dependent, therefore, upon the partition coefficient which determines their distribution in a mixture of water and lipoid substance."

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** National Research Fellow.

[1] De Med. Mat., Lib. 4, 76; 7, 207.

The work of F. A. Bucholz[1] had shown that many substances could behave like narcotics although, chemically, they were entirely foreign to being classed as narcotics of the alkaloid type. Further, this action ran parallel to the fat-solubility of these substances. This evidence supports the first postulate of the theory. The second postulate is supposed to be accepted upon the grounds of common experience, that narcosis is confined to the lipoid-containing tissues. The third postulate is demonstrated by the work of Baum[2] in showing that there is a pronounced parallelism between the distribution coefficients and the degree of narcosis. This relation is shown in Table I, the threshold values being for tadpoles.

TABLE I

Substance	Distribution Coefficient	Threshold value in Mol/Liter
Trional	4.46	.0018
Tetronal	4.04	.0013
Sulfonal	1.11	.0060
Bromal hydrate	.66	.0020
Chloral hydrate	.22	.020
Ethyl urethane	.14	.040
Methyl urethane	.04	.400

A great deal of research has been done on this part of the theory. One very striking example, that deserves mention, was carried out by Moral.[3] It is known that the distribution coefficients are not independent of the temperature and that the values may either decrease or increase, as the temperature rises. Moral showed that, if this occurred, then the degree of narcosis was altered just as the theory predicted.

TABLE II

	Temp. −3°		Temp. 30°−36°	
Substance	D. Coef.	Rel. Strength	D. Coef.	Rel. Strength
Salicylamide	22.23	1300	14.00	600
Benzamide	.672	500	.437	200
Chloral hydrate	.053	50	.236	250

However, in spite of such supporting evidence as this, there have developed some very important objections. First, the theory in reality only defines the physical properties which a narcotic must have. Overton's explanation that the cell membrane is altered is not satisfactory, for it is known that during narcosis the permeability is first lowered and then increased. This seems to be an effect rather than a cause. Meyer's later assumption,[1] that solution of the narcotic in the lipoid would disturb the functional activity of this substance, is indefinite and gives no clear picture of what has happened within the cell.

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[1] Inaug. Diss., Marburg (1895).

[2] Arch. exp. Path. Pharmakol., 42, 119 (1899).

[3] Arch. ges. Physiol. (Pflüger's), 171, 469 (1918).

The lipoid solubility does not seem to be the important factor in all cases. The grey substance of the brain contains 8.5% lipoid, and the white matter 16%.[2] Kochmann points out that, in spite of this, narcosis starts much sooner in the gray matter and is stronger than the narcosis in the white matter. Then Winterstein showed that narcotics were capable of exerting their typical effects on organisims that were free from lipoids (e.g., acetone-extracted yeasts). Also, the well-known effects of many narcotics on enzymes could in no way involve lipoid material. So the idea that lipoids are an essential factor in narcosis is wrong.

Attention must also be called to the fact that too great an importance cannot be attached to the distribution coefficients. Superficially, they do run parallel to the strength of the narcotic but there are many exceptions. Monoiodoisovalerylurea has a distribution coefficient of 1.05 but is inactive as a narcotic although one would predict from the distribution coefficient that it would be as active as sulfonal. Then the distribution coefficients of caffeine and theobromine[3] are such that they should be good narcotics but these drugs have an effect just the opposite from a narcotic and behave as stimulants. Furthermore the distribution coefficients are measured for distribution between olive oil and water and not lipoid and lymph.

The experiments of K. H. Meyer and Gottlieb Billroth[4] were very important in spite of the numerous mistakes. They were determining the concentration of inhalation narcotics necessary to produce narcosis in mice. The concentration of the narcotic in the brain lipoids was dependent upon the concentration of the narcotic in the inhaled air. The body fluids were merely passages for the narcotic to reach these structures. The rapidity with which the threshold values were reached depended upon the solubility of the narcotic in the body fluids. The more insoluble narcotics required greater lengths of time to become effective. From this point of view, the theory is rather a theory of *transportation.*

This offers an explanation of the fact that the higher homologs of some narcotics are inactive, although the distribution coefficients are much greater than those of the lower members of the series. It is simply that the water solubility has been so reduced that the substance cannot be transported to the cells faster than these can eliminate them, so a concentration of the narcotic sufficiently great to produce narcosis is never reached.

The foregoing interpretation of the Meyer and Overton theory as a theory of transportations is essentially that outlined by Kochmann.[5] Kochmann's views seem to make a worthy contribution to the subject but one feels that there is something of greater significance to the distribution coefficients than he has indicated. For the distribution coefficients run parallel to the strength of the narcotic to a much greater degree than the rapidity with which they become effective. If it is considered that the tendency to be concentrated in the oily layer in preference to the aqueous, is a *crude* measure of the extent of adsorption on the colloids of the nerves, it is clear why the strength of the narcotics should be roughly related to the distribution coefficients. In ordinary adsorption there is a partition of the substance between the solvent and the insoluble substrate. It is surprising that the analogy holds as well as it does.

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[1] Wiener med. Wochenschr. No. **27** and **28**. Sonderdruck (1921).

[2] Compt. rend. soc. biol., **62**, 1153 (1907).

[3] Arch. farmacol. sper., **38**, 59 (1924).

[4] Z. physiol. Chem., **112**, 55 (1921); Münch. med. Wochenschr., **8** (1921).

[5] "Handbuch. exp. Pharm.," **1**, 449.

Traube's theory of narcosis,[1] is similar in many respects to the Meyer and Overton theory. Traube has gathered an immense amount of data on the surface tension of solutions of narcotics and has applied this to possible methods of distribution within the cell. His data are useful in showing that the narcotics are not necessarily in solution but are adsorbed and that such colloidal phenomena play an important rôle in narcosis. It was demonstrated by his work that the strength of a narcotic was related to the surface tension of a solution of the narcotic as Table III shows:

TABLE III

Substance	Threshold value in Mols.	Cap. elevation of ¼M. sol.(H_2O 9.15)	Mol. Conc. of iso-cap. sol.
Methyl alcohol	.57	88.6	14.
Ethyl alcohol	.29	84.0	5.
n-Propyl alcohol	.11	74.0	1.6
i-Butyl alcohol	.045	56.5	.46
n-Butyl alcohol	.038	—	.45
Active amyl alcohol	.023	37.4	.14

There is a distinct parallelism between the surface activity of a narcotic and its physiological action, solutions that are iso-capillary are of the same degree of toxicity, etc. Then one can predict, roughly, the effect of isomerism and homology in drugs from a knowledge of the surface activity. What Traube has really shown is that the lowering of the surface tension can be substituted for the Meyer and Overton distribution coefficient. This does not help the theory very much but does get around the fact that lipoid-free organisms can be narcotized, for the surface activity of the narcotic does not depend upon the lipoids.

In accordance with the work of Gibbs it is known that if a substance concentrates at an interface, or is adsorbed, the surface tension at the interface is lowered. Furthermore, the degree of lowering of the surface tension is a function of the extent of adsorption. It must not be forgotten that the interface at which Traube measured these surface activities was the liquid-air interface while the important interface in the cell is the liquid-colloid interface. His data cannot be expected to be of universal applicability; it is remarkable that the relation holds as well as it does. As mentioned above, the adsorption is only a preliminary phase, and narcosis or toxic effects do not necessarily follow. For it is known that amino acids and sugars are adsorbed but do not behave as narcotics. This adsorption, doubtless, aids the transportation of the narcotic to the cell and facilitates its entrance into structure but does not explain the effective mechanism of narcosis.

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[1] Arch. ges. Physiol. (Pflüger's), **153**, 276 (1913); **160**, 51 (1915); **161**, 530 (1915).

Verworn has studied the oxygen metabolism of varied organisms while they were under the influence of narcotics and upon the results of his experiments put forth a theory of narcosis.[1] Verworn's hypothesis is that the loss of response to stimulation is due to the disturbance of the oxygen metabolism. This theory is very often referred to as the "suffocation" or "asphyxiation" theory but it should be pointed out that the asphyxiated state does not occur by excluding oxygen from the cell but arises through the inhibition of the oxidation process by the narcotic. Verworn assumed that the oxygen carriers were in some way related to the lipoids, thus attempting to reconcile the theory of Meyer and Overton with his.

In general, it is true, that during narcosis there is a lowering of the metabolism; but many workers have shown that this is not always the case. Loeb and Wasteneys,[2] in an investigation on sea-urchin eggs, showed that potassium cyanide must decrease the oxidation about two-thirds before the development was hindered, while narcotics such as chloral hydrate, chloroform, ethyl urethane, and alcohol could bring about the same degree of hindrance without materially altering the oxygen consumption. Then Winterstein[3] showed that ethyl urethane when applied to the spinal cord of the frog caused a marked decrease in the oxygen consumption, while ethyl alcohol caused just the reverse under the same conditions. There are a number of organisms that exist without the aid of atmospheric oxygen, the intestinal worm Ascaris is such a one. Winterstein has shown that this worm can be narcotized. Verworn's theory cannot explain this.

However, it must be pointed out that these are just a few of the exceptions which show that any alteration in the oxygen metabolism is not the cause of narcosis but rather an effect.

M. Kochmann[4] presents a rather interesting but inadequate theory of narcosis. It grew out of the observation that many of the common narcotics would inhibit the swelling of various substrates, such as fibrin, in water or dilute salt solutions. This action was found to be reversible and Kochmann felt that it must be the cause of narcosis. The mechanism of this is explained in Kochmann's own words: "Thereby lowering the permeability of the cell membrane which amounts to a diminution and inhibition of the total exchange of material and consequently to a stop of the cell function, or in other words it means the narcosis of the cell." The idea is not new. This is the old alibi of practically all previous workers when they are forced to a definite statement of the cause of narcosis. In fact, this does not explain narcosis but blames the phenomena on something else which in itself is indefinite and has been shown to be an accompanying phenomenon to narcosis and not its cause. What Kochmann has really shown is that narcotics under certain conditions will partially dehydrate some colloidal substances.

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[1] "Narkose" (1912).

[2] J. Biol. Chem., **14**, 517 (1913).

[3] Biochem. Z., **61**, 81 (1914).

[4] Heffters "Handbuch exp. Pharm.," **1**, 449.

Narcosis is not the simple problem that it was once thought to be, for there are many changes taking place in a tissue under the influence of narcotics. Some of these changes are characteristic of only one tissue; the true explanation must point out the phenomenon that is common to all cases. None of the above theories do this; it seems that in each case the observations were confined conclusively to some one of these changes. Consequently, the theories based upon such data are partially right, although they contradict one another in many details. It is the intention of this paper to indicate the basic phenomenon back of all cases of narcosis and to show that the other changes are just some phase of this general phenomenon.

A few of the earlier workers in the field of narcosis foresaw that colloid chemistry undoubtedly would be associated with the phenomena and consequently proposed theories that related to coagulation. Probably the first of these was the theory of Binz.[1] This theory was concerned with the effect of narcotics on the brain. The author showed that brain tissue exposed to dilute morphine hydrochloride solutions would undergo coagulation and that the initial stages of this phenomena were reversible. If the narcotic was allowed to act for too great a time the coagulation was irreversible. The ganglion cell was supposed to be the point of attack of the narcotic agent and if the material was not irreversibly coagulated the cell would return to normality, or if it was in the advanced stage where the protoplasm had become "granulated" then death was inevitable.

Another theory that resembled Binz's theory was proposed by Claude Bernard.[2] This theory was based upon the "semi-coagulation" of the protein constituents of the cell as the cause of narcosis. Although Bernard was not the first to propose such a theory he was the first to investigate its possibilities and to formulate and explain the mechanism on an extensive scale.[3]

The views of Claude Bernard have been expressed by many, but for the sake of clearness the following paragraphs translated from Bernard's "Leçons sur les Anesthésiques" are quoted to cover the important phases of his theory.

"The action of anesthetics is very general. They react not only with animals but also with plants. Thus they stop the movements caused in sensitive plants by external stimuli, the movements of the anthers of some flowers for instance.

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[1] Deutsche Klinik, Nr. 29, 277 (1860).

[2] "L'Anesthésie." Union med., Paris, 8, 109 (1869).

[3] "Leçons sur les anesthésiques et sur l'asphyxie" (1875).

"Ether and chloroform have been used by veterinarians or by physiologists with almost all animals. These were used at first with the large animals, horses, cattle, sheep, etc., but especially with horses. Ether and chloroform are not now used with cattle or sheep if the operation is a serious one. The veterinarians gave up the use of these anesthetics very quickly, because of a fact which had nothing to do with the scientific side. The flesh of animals anesthetized by ether or chloroform has an unbearable taste which prevents selling the flesh as butcher's meat in case the animal dies under the operation.

"It is clear that an animal put under the influence of chloroform cannot be considered normal. It is being treated with a toxic agent, the action of which is usually not carried to the point of killing the animal; but which nevertheless modifies considerably the physiological functions of the organism. That is so true that the most violent poisons may be absolutely without effect on an animal which is anesthetized with chloroform or ether.

"There are two successive and perfectly distinct, or rather opposed phases in the state of cerebral circulation under the influence of anesthetics. The first phase corresponds to the experiments in which we found hyperaemia; the second to the experiments which showed the brain in a state of anaemia. I insist on these contradictory experiments because it is necessary to explain them by different conditions as we have just done in this case.

"The hyperaemia corresponds to the agitation which marks the beginning of the administration of the anesthetic; but it is not a special point, because one can produce it in other ways, for instance merely by making the animal scream. We have already seen that this agitation, observed in the first stages of the administration of chloroform or ether, corresponds to a special irritation quite distinct from the anesthetic effect, and in this first stage there occur phenomena quite foreign to anesthesia.

"On the other hand, during the period of dropping-off and complete insensibility, which is that of true anesthesia, we observe an anaemia more marked than the normal state. We have pointed out in the first lecture that this result agreed perfectly with what we knew in regard to the relative states of the circulation when organs are functioning or resting. During their period of activity, the organs receive much blood; during their period of rest, they receive much less. Anesthesia, being the suppression of sensitiveness, represents certainly a state of absolute rest for the sensory nervous system, and it is therefore perfectly natural that this should be accompanied by anaemia of the brain.

"I do not believe that the cerebral anaemia which we have observed is sufficient to account for anesthesia. It is true that during anesthesia the brain contains a little less blood than under ordinary conditions; but this circulatory decrease does not exceed that of an organ at rest. In the brain there is still quite enough blood to sustain the nervous functions and to permit the sensory system to react to external stimulants as it would do in a state of normal rest. Then, too, the blood of an anesthetized animal contains quite enough oxygen to produce the ordinary effects, since some analyses of the blood under these conditions have even shown a larger percentage of oxygen than the normal.

"There is, therefore, something besides cerebral anaemia to anesthesia. We have had to raise this point in order to make certain that this is not the proper line of attack on the problem of anesthesia.

"I believe that anesthesia depends immediately and directly on the presence of chloroform in the blood and on its special action on the nerves. The vascular changes are only secondary accompaniments of the phenomenon and not the cause of it. To ascribe anesthesia merely to an anaemia of the brain would be the same thing as considering drunkenness merely as a result of the general change in vascular conditions which are always noticeable. There is certainly something more than that. Drunkenness depends on the alcohol in the blood and on its direct action on the nerves; it is the same for anesthesia which has some things in common with drunkenness.

"I have shown you experimentally that heat will anesthetize frogs perfectly. That, after all, is in harmony with what we know in regard to vital properties in general and to those of the nervous system in particular. At a low temperature, at 0° and even a little above it, a frog benumbed by the cold remains completely insensitive to external influences; at this temperature it is only slightly sensitive, and sometimes completely immune to the actions of the most energetic poisons. As the temperature rises, the sensitivity increases and the frog becomes more and more susceptible to toxins, etc.

"The grand sensory nervous center, the center of centers, is the brain. As such, it reacts on the spinal cord—which plays the part of a nerve with reference to the brain although it is itself a center with reference to the nerves—in the same way that the spinal cord in its turn reacts with the sensory nerves. For anesthesia to occur, it is necessary for ether or chloroform to come in contact with a nervous center. When this condition is fulfilled, anesthesia results in all parts of the nervous system under control of the nervous center affected, except the sensory system of the respiratory and circulatory functions essential to life.

"Without committing ourselves to the nature of the action produced on the nervous center itself, we will prove that there is a special selective action, dealing exclusively with the sensory nerves of the nervous system. Here is a frog which is completely anesthetized. You will note that there are no voluntary movements, that it is quite insensitive to external stimulants, and that it remains absolutely inert even when pinched violently. Nevertheless, the motor nerves in this frog have kept their ordinary excitability.

"To show this, let us bare the sciatic nerve, a mixed nerve which corresponds both to a sensory trunk and to a motor trunk. The sensory fibers are anesthetized; but the motor fibers keep their normal properties. If we excite the nerve with an electrical current, we shall produce movements in the corresponding foot, just as we could have done with a normal frog. Thus the chloroform, which diffuses through the spinal cord produces anesthesia and only destroys the properties of posterior sensory roots without affecting the anterior motor roots. I will not say that this is a very startling fact, because analogous cases are known; but it is a very remarkable fact and one which deserves the whole attention of the physiologist.

"We have seen that anesthesia can be produced by a great number of ways or reagents: chloroform, ether, hot water, anaemia, asphyxiation, etc. Does this mean that there are many different kinds of anesthesia? No, they are only different methods of producing anesthesia, and the final mechanism must be the same in all cases. We have just shown that they all act in the same portion of the organism, on the sensory cell.

"Let us begin by summing up the effects of anesthetics in approximately the order in which we have studied them:—

(1). An anesthetic is a volatile substance which gets into the blood in the case of the higher animals through the respiratory surfaces. Since the anesthetic is readily adsorbed, it penetrates rapidly. From the beginning of inhalation we find chloroform in the blood, even though a single whiff has been taken. The blood, which takes up the anesthetic, conveys it to the nervous center on which it acts. We have confirmed this previously-stated opinion by direct experimental tests. We have also shown that in the nerve centers anesthesia is not accompanied by congestion, as people had hitherto assumed, but by a relative anaemia.

(2). Are the nerve centers all affected at the same time by the action of the chloroform? No, the brain is affected first—one loses first the consciousness of the ego, the recognition of external phenomena. The spinal cord is not affected until later and one can even distinguish several periods in the action of chloroform in this nerve center. At the beginning of the anesthetic action the reflex movements having their center in the medulla oblongata and in the spinal cord continue to function and are even more energetic and rapid. Then these centers are affected and the reflex movements disappear gradually; but the movements which would be voluntary if the animal had not lost consciousness persist for some time; finally, they also stop and the animal falls into a collapse with complete muscular relaxation. It becomes as motionless as a corpse. The respiratory movements and the movements of the heart alone remain.

"What picture ought we to make of the action of chloroform on the central nerve cell? All the effects produced on an anatomical unit, no matter what they are, can only take place through a physical or chemical modification of of that unit. We can no longer postulate mysterious actions to which we ascribe the word *vital*. When we employ this word it means that we know nothing definite about the phenomenon in question. For a certain number of the toxic actions we are able today to determine definitely the physical or chemical phenomenon which is the cause of the action. Thus carbon monoxide reacts with the red blood corpuscles, combining chemically with the haemoglobin. The demonstration of this chemical action is easy to make and one can produce the compound *in vitro* as well as *in vivo*.

"We are not so advanced as to the action of anesthetics; but we believe that a certain number of arguments based on an exact analysis of the facts will enable us to form a fairly definite idea of the way in which anesthetics act on the nerves. It seems to us that this action consists in a semi-coagulation [Bernard means what we should call a slight, reversible coagulation of the bio-colloids] of the substance itself of the nerve cells, a coagulation which would not be permanent, the anatomical unit being able to return to its normal state after the toxic agent is eliminated.

"To understand this action as postulated, let us remember that chloroform does not act solely on the nerve tissues. Far from that, it has an action on all the tissues and attacks each one at a time which is a function of its susceptibility. Just as chloroform affects birds very rapidly, and frogs and plants slowly, in the same way it will affect one set of tissues in a given animal before another set. The effect shows itself with the other tissues after it has become noticeable with the nerve tissues, the most delicate of all. The plant has no nervous system and yet chloroform and ether act just as fatally on it and stop the activity common to all its anatomical units. With the sensitive plant, for instance, the anesthetic affects at first the irritability of the cells, destroying thus the movements of the leaves. An anesthetic is not a special poison for the nervous system. It anesthetizes all the cells, benumbing all the tissues, and stopping temporarily their irritability.

"We can study elsewhere than in the central nerve cells the phenomenon which causes this stoppage of action and which we consider as a coagulation or as a beginning of coagulation. If we place a muscle in the vapor of chloroform or ether, or if we inject into the muscular tissue some water containing a little chloroform or ether, and if we let this stand for quite a while, the muscle becomes rigid. The content of the fibers has coagulated and we have what is called the chloroform rigor. If we let the chloroform act for a shorter time, we reach a point where the muscle loses its irritability, and is anesthetized. If at this moment we examine the muscular fiber under the microscope we see that it is no longer transparent and that it is in a state of semi-coagulation. . . .

"It is permissible to assume that something similar happens in the nerve cell; but the latter is much more delicate and much more susceptible to the action of chloroform. It is the portion which first undergoes coagulation. As the chloroform is carried away by the blood, it returns to its normal state, coming out of its anesthesia as the muscle comes out of its rigidity."

Since the time of Claude Bernard no one has made any serious attempt to "modernize" these earlier colloidal theories. In fact just the reverse has taken place, for such workers as Winterstein and Kochmann criticize the theory severely and deny any important value to it.[1] The criticism offered by Winterstein, which may be taken as typical, does not seem justified in the light of modern knowledge.

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[1] Winterstein: "Die Narkose" (1919).

First let us define the terms "narcosis" and "narcotic." The definition of the German workers is accurate enough: narcosis is the state of a living cell during a reversible paralysis and a narcotic is a substance that will bring about this condition.

There are three basic criticisms directed against the coagulation theory:

(a) The concentrations at which narcotics are active are much less than that required to flocculate the cell colloids.

(b) Coagulation of the cell colloids represents the toxic effect of a narcotic and is irreversible, whereas narcosis is a reversible phenomenon.

(c) The cases in which the dispersion of the colloids is decreased by narcotics are explained as being only apparent.

The objection that the concentration of narcotics during narcosis is too low to produce any decrease of dispersion is not convincing. This conclusion was reached by determining the concentration of narcotics in the blood and different organs during narcosis. The following table from Niclaux[1] is typical of such analysis. The values are given in mgs. per 100 gm. substance and are the quantities found in the organs of a dog. These are upper limits, for they are the amounts found in the organs just after death had occurred, due to the action of the narcotic.

TABLE IV

Organ	Chloroform	Ether
Arterial blood	70–64	161–175
Venous	52–49	160–169
Liver	47–52	102–139
Kidneys	39–46	125–140
Spleen	21–38	107–132
Muscle	15–24	100–120
Brain	46–59	153–163

For these and similar data one is not justified in drawing the conclusions that form the basis of this criticism, for we know that an increase in the distribution coefficient of the narcotic runs parallel to an increase in strength, or what is almost the equivalent, the lower the solution tension in the body fluids, the greater will be the tendency to be adsorbed by the tissues. The mere determinations of concentrations of narcotics in body fluids have no meaning, for the adsorption coefficients are unknown, and the amount of adsorbent is, at the present, indefinite; so that it is impossible to calculate the extent of adsorption. The values obtained for the different organs are just as useless, for they give no information concerning the distribution within the organ. However, the brain is an exception that offers a crude possibility, for the narcotic is adsorbed in the lipoid material. Then from a knowledge of the amount of lipoid material in the brain, one can calculate the amount of narcotic per unit amount of lipoid. The following material in the Table V is a collection of several values from independent workers.

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[1] Compt. rend. soc. biol., **60**, 206 (1906); Compt. rend., **144**, 341 (1907).

TABLE V

Substance	Amt. in 100 gms brain	Amt. in Millimols per 1000 gms lipoid	Author
Ether	.117	132.	Storm van Leeuwen[1]
Chloral hydrate	.0112	22.	Archangelsky[2]
Adalin	.0112	4.	
Bromural	.0111	4.	Kwan[3]
Neuronal	.0194	8.	
Alcohol	.327	591.	Giebant[4]
Chloroform	.035	24.	

Battelli and Stern[5] have produced important evidence that narcotics are only effective as such when they are in the approximate flocculating concentration. The oxidizing enzyme in the liver that oxidizes succinic acid can be easily narcotized by the common narcotics. The nucleo-proteins of the liver probably serve as the substrate upon which the enzyme is dispersed. Table VI shows the close agreement between physiologically active concentrations and the flocculating concentrations.

TABLE VI

Substance	Molar Concentration which: inhibits oxidation	Molar Concentration which: flocculates nucleo-protein	Substance	Molar Concentration which: inhibits oxidation	Molar Concentration which: flocculates nucleo-protein
Methyl alcohol	5.78	6.31	Methylethyl ketone	.82	.94
Ethyl alcohol	2.97	3.33	Methylpropyl ketone	.34	.39
Propyl alcohol	1.09	1.44	Ethyl urethane	.95	1.06
i-Butyl alcohol	.41	.46	Propyl urethane	.39	.48
i-Amyl alcohol	.18	.24			

The criticism that small amounts of narcotics would not flocculate is based upon observations of protein sols and other bio-colloids when treated with reagents "in vitro." The assumption that is tacitly made is that the material is in the same state as when in the cell. This is not likely.

It is well known that rather large amounts of alcohol are required to flocculate protein sols. Now if such a sol is treated with a small amount of electrolyte the amount of alcohol required to bring about the flocculation is less.[6] If enough electrolyte is added, the flocculation concentration of the alcohol can be made very low. For example a slightly acidified albumin sol was treated with sodium sulphate until it was on the verge of precipitating; one drop of the common alcohols or a small crystal of chloral hydrate was then sufficient to bring about flocculation.

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[1] Arch. ges. Physiol. (Pflüger's), **165**, 594 (1916).
[2] Arch. exp. Path. Pharmakol., **46**, 347 (1901).
[3] Arch. intern. Pharmacodynamie, **22**, 331 (1912).
[4] Compt. rend. soc. biol., **127**, 746 (1899).
[5] Biochem. Z., **52**, 226 (1913).
[6] Cf. Gurchot: J. Phys. Chem., **30**, 83 (1926).

Other proteins were investigated by this method. Edestin, when treated with electrolytes and alcohol, was found not to be sensitized as much as the albumin. The proteins of wheat flour when examined by this method were found to be relatively indifferent towards the common alcohols but show a slight decrease in dispersion when treated with chloroform. This shows that this sensitization is specific both for the different narcotics and substrates and is in line with the fact that all narcotics do not affect the same tissues equally.

The phenomena of sensitization are not characteristic only of the acidified albumin sols and sodium sulphate. For example a slightly alkaline albumin sol required 0.8 cc of alcohol to produce a marked turbidity in a given volume of the sol. The same volume of sol when treated with 3.6% of calcium chloride required only 0.2 cc to produce the same degree of turbidity. Thus in this experiment the addition of a small amount of calcium chloride has made the sol four times as sensitive as the original sol to the effects of the alcohol.

It is quite possible that some of the colloidal systems of the cell may in an analogous manner be so sensitized that the addition of a small amount of a narcotic will flocculate them. The living cell contains such a great variety of organic matter that the possibility of such a condition is very probable. If such a state exists, then low concentrations of narcotics would easily flocculate the colloids.

Any doubt about the existence of such critical states is dispelled when one considers the ionic antagonism in biological systems. Very small amounts of the different electrolytes bring about profound reactions in the protoplasm. There is evidence that other such critical states exist, and the phenomenon may be quite general. Pickering and Hewitt[1] suggested that the initial phases of blood coagulation are a physical process and find that it is reversible. They also demonstrated that this system was made very sensitive by other substances that were present in the blood.

The coagulation temperatures of pure proteins is in general above 50°. Heilbrunn states that "the description of any protein which coagulates at 30°-40° is rather doubtful." Yet there are many cases known where death can be brought about at lower temperatures e.g., Phyllopods at 18°-10°[2] and cuttle-fish sepia at 28°.[3] Heilbrunn[4] found that the protoplasm of sea-urchin eggs was coagulated at 32°-33° and that emulsified fats or lipoids, that were present, were related to this sensitization. Other workers have found that lecithin has a decided influence on the coagulation of proteins.[5] So it is not at all impossible that many colloidal systems of the living cell are in a critical state.

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[1] Biochem. J., **15**, 710 (1921).

[2] Sitzungsber. Akad. Wiss. Wien., **75**, 583 (1877).

[3] "Action de la chaleur et du froid" (1919).

[4] Am. J. Physiol., **69**, 190 (1924).

[5] Lloyd: "Chemistry of Proteins."

In making studies on the coagulation of protoplasm, it is well to remember that the coagulation often brings about no visible microscopic change. The protoplasm seems to "set" like a jelly. In experiments on isolated proteins enough reagent is generally added to produce the typical coagulation that can be seen with the eye. The conclusion that such coagulated proteins are similar to coagulated protoplasm is not justified. Many workers seem to overlook this difference and this may be a reason for much of the conflicting data on the reversibility of coagulated or semi-coagulated biological systems. Where there is no visible change produced, an investigation of the viscosity variation is helpful. The changes in the viscosity of coagulating protoplasm are quite characteristic. The initial stages of coagulation are associated with a phase of lowered viscosity which passes through a minimum and goes above normal as the coagulation progresses.

The second objection, that coagulation is irreversible and represents the toxic action, and the third objection, in which the lowering of the dispersion in known cases is made to appear as being only apparent, must be considered together as they are obviously related. In order that Winterstein's criticisms be coherent and complete, it was necessary to explain the known cases of the lowering of dispersion of the cell colloids as being only apparent because this was found to be reversible. Then since he thought that coagulation was irreversible, he had to consider the two cases separately.

The objections to the decrease in dispersion of the colloids are groundless. Winterstein admits that this phenomena is "probably reversible" but attempts to show that the phenomenon is only apparent and in actuality is not a decrease in dispersion. He attributes the phenomenon to the type of turbidity (decrease in dispersion) that was obtained by Calugareanu[1] in lecithin, chloroform and water emulsions. Calugareanu found that the emulsion in this case was reversible upon the removal of the chloroform phase. This could be effected by warming until the chloroform has volatilized, or upon standing so that the chloroform merely evaporated. The emulsion was obtained by dissolving lecithin in either chloroform or water, then to this solution the other liquid was added until its solubility is exceeded so that there are two layers. Calugareanu observed that at the dineric interface the solutions became turbid and, if allowed to stand long enough, the turbidity extended further into the liquid. The same effect could be brought about more rapidly by shaking. The interpretation of this phenomenon that was offered by Calugareanu and accepted by Winterstein is entirely wrong. They believed that the colloidal lecithin particles adsorbed the chloroform very strongly, thus forming an outer shell around the micellae. This decrease in dispersion is then only apparent.

The type of emulsion that Calugareanu obtained is well known to colloidal chemistry and depends upon the adsorption of the lecithin at the dineric interface. It is known, from the Gibbs equation that if the lecithin lowers the surface tension at the chloroform-water interface it will be concentrated at that place. Then according to Bancroft,[1] Gibbs[2] points out that if we call the two liquids A and B, and the film C, we have to consider two surface tensions, the one at the contact A and C, and the one at the contact between B and C. If the surface tension at the water-emulsifying agent interface is less than that at the oil-emulsifying agent interface, the films will tend to curve so as to convex on the water side and we shall have a tendency to emulsify oil in water.[3] If the surface tension at the oil-emulsifying agent interface is lower than the surface tension at the water-emulsifying agent interface, the film will tend to curve so as to be convex on the oil side and we shall have a tendency to emulsify water in oil.

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[1] Biochem. Z., 29, 96 (1910).

"The simplest general formulation—which we owe to Briggs[4]—is that we get oil-in-water if the emulsifying agent at the interface is chiefly in the water phase and water-in-oil if the emulsifying agent at the interface is chiefly in the oil phase. A couple of illustrations will make this clear. If we start with a water-soluble colloid which is strongly adsorbed at the interface, but is not peptized markedly by the oil, we should expect to emulsify oil in water. If we start with an oil-soluble colloid, which is adsorbed strongly at the interface but is not peptized markedly by the water, we should expect it to emulsify water in oil. As a matter of fact, an overwhleming majority of emulsions come in this class. Since most emulsifying agents will not peptize the second liquid by themselves, it is usually necessary to break up the liquid into fine drops by some form of mechanical agitation."

The observations of Calugareanu were not original; the phenomena had also puzzled Winkelblech[5] at an earlier date.

This type of emulsion is exceedingly improbable in the living tissue, because to produce the dineric interface a concentration of the narcotic sufficient to exceed its solubility in the plasma is necessary. It is known that the concentration of narcotics necessary to produce narcosis is less than enough to saturate the tissues. Even Winterstein himself objects to any theory that requires a high concentration of narcotic to bring about the reaction.[6]

According to Gwathmey[7] in Binz's experiments "fresh sections of the brain cortex of rabbits were placed in a one per cent morphine hydrochloride solution, or exposed to chloroform vapors. The effect of coagulation narcosis was produced, as is seen when protoplasmic poisons of neutral reaction are allowed to act upon large transparent infusoria. The protoplasm at first darkened, and the movements became sluggish; later on the protoplasm becomes granulated, and the movements cease. Recuperation may take place from the first stage, by washing away the poisons, but not from the last stage. The first stage is likened by Binz to the sleep of the cell; the last to death. The first trace of coagulation may redissolve but coagulation itself does not. "Also in regard to Claude Bernard's theory," in his opinion, the mechanism is always the same, in spite of the difference of the narcotic agent; for they all produce one identical modification in the ganglion cell. This modification of the ganglion cell consists in a "semi-coagulation" of the protoplasm of the nerve cell, this semi-coagulation being merely transitory, the protoplasm resuming its previous state after the removal of the narcotic agent from the cell. This view was derived from the rigidity of muscle fibers after exposure to chloroform vapors."

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[1] Bancroft, "Applied Colloid Chemistry," 352 (1926).

[2] Gibbs: "Scientific Papers," 258 (1906).

[3] J. Phys. Chem., **17**, 515 (1914); **20**, 407 (1916).

[4] Briggs: Unpublished work.

[5] Z. angew. Chem., **18**, 1953 (1906).

[6] "Die Narkose," 256 (1919).

[7] "Anesthesia" (1914).

These older experiments were carried out with concentrations of reagents that were not excessive and they confirm the statement that in the stage of decrease of dispersion the phenomena is reversible, but becomes irreversible if coagulation has gone too far. As a matter of fact, Winterstein is wrong in considering that the decrease in dispersion is a phenomenon separate from coagulation. This decrease in dispersion is a preliminary stage of coagulation and is reversible as Binz and others have shown. Whereas if the narcotic is allowed to act in greater amounts or for a longer time a granular coagulation will set in and this is irreversible. This is in agreement with the fact that narcosis cannot be maintained for an indefinitely long time without serious consequences or that narcotics in high concentrations are toxic.

The coagulating action is "freely objected to" because colloidal protein sols are irreversibly coagulated by narcotics.[1] It is quite true that the coagulation of proteins or other bio-colloids often seems irreversible. However the coagulation by narcotics is a different matter because the coagulated proteins are, under certain conditions, reversibly peptized as can be shown.

In the experiments where the protein sols were sensitized by ether to electrolytes it was found that at the beginning of the decrease in dispersion the phenomenon was reversible. That is, if the ether is removed by blowing a stream of air through the solution, the turbidity is decreased. At a later stage when the albumin has been precipitated, the precipitate can be removed by filtration and partially repeptized in a solution of the same composition as the original except that the ether is absent. This peptization becomes increasingly difficult if the ether is allowed to act for longer lengths of time.

As a matter of fact, this type of experiment will also illustrate the invalidity of Winterstein's explanation of the reversible lowering of the dispersion. If the albumin sol is treated with sodium sulphate, as described above, and more of one of the higher alcohols (amyl or butyl) is added than is truly soluble a very voluminous precipitate will be produced. This is an emulsion of the type Calugareanu obtained, and upon shaking appears at once without the preliminary turbid stage. However, if an amount of alcohol is added so that it is in true solution, the formation of the precipitate is much slower and passes through the preliminary turbid stage. In this case an emulsion is impossible. The explanation of the precipitate produced by large amounts of alcohol depends upon the fact that the albumin is adsorbed at the water-alcohol interface and forms an emulsion upon shaking.

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[1] "Die Narkose," 257 (1919).

It is important for the colloid theory of narcosis to make certain that reversible coagulation does take place during narcosis. As noted above, the coagulation of protoplasm is frequently marked by no visible change. Consequently it is highly desirable to attempt to follow such changes by other methods. A method that would indicate such changes is known and has been applied in certain cases. The changes in viscosity of living protoplasm undergoing narcosis have been followed in the cell and afford highly interesting data. Weber[1] has made extensive studies on the viscosity of the protoplasm of Spirogyra by means of the sedimentation velocities of particles within the cell when placed in a centrifuge. Also, Heilbronn[2] made observations on the resistance offered by plant protoplasm to falling starch granules when sections of the tissue were rotated through an angle of 180°, the material being subjected to varying concentrations of ether. Heilbrunn,[3] in a manner similar to that of Weber, followed the viscosity changes of protoplasm during coagulation by heat.

The most trustworthy data agree that there are two distinct phases in change. At low concentrations of the narcotic, or a slight elevation of the temperature in the case of Heilbrunn's study, there is a decrease in the viscosity which passes through a minimum and then increases above normal. The viscosity changes, when properly interpreted, show the varying degree of coagulation. Since the narcosis is produced by the slight, easily reversible coagulation it is found that the narcosis occurs in the stage of decreasing viscosity, as one would expect.

Before going into greater detail on the relation of coagulation to narcosis let us examine some of the theories and state clearly their shortcomings. No theory, except the colloid theory, offers a mechanism of narcosis that is common to all cases and can be adapted to direct experimental proof. It is a recognized fact that narcotics in low concentrations behave as stimulants; other theories are not able to offer any good explanation of this, and in most cases it is ignored. Nevertheless it is a definite part of the problem and an adequate theory must make a working explanation. The problem of recovery, from the effects of the narcotic, has no satisfactory treatment at the hands of other theories. The toxic effect of narcotics, when in high concentrations, must also fit in the theory of narcosis and agree with modern concepts of toxic action. A very outstanding deficiency of other theories is their inability to account for the type of narcosis produced by physical means such as a blow, heat, cold, and electricity. This deficiency becomes more pronouned in explaining the local anesthesia produced by water. The cases of narcosis produced by hydrocyanic acid and magnesium sulphate are also difficult to reconcile on the basis of any of the other theories.

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[1] Biochem. Z., **126**, 21 (1921).

[2] Jahrb. wiss. Botan., **54**, 335 (1914).

[3] Am. J. Physiol., **69**, 190 (1924).

These are the outstanding phases of the problem of narcosis. Obviously, they are related to each other for the same narcotic can bring about several effects. An adequate theory must relate these parts coherently and explain them on a common basis. Henderson[1] has given a summary of our knowledge of anesthesia at the end of 1929 which may be of value for people who wish to get the literature references. It cannot be called an adequate critical presentation.

The most obvious thing about the living cell is the colloidal character of its constituents and the extreme sensitivity to changes of this colloidal state i.e., ionic antagonism, etc. Since the criticisms of the colloid theory have been found to be groundless it is desirable to re-examine the evidence and attempt to explain the above phenomena upon this basis.

This flocculation by small amounts of narcotics is stated as a fact and exists independent of any explanation whether it is right or wrong. However, it is beneficial to have some some sort of explanation as it makes us feel that we understand the problem better, because it enables us to draw a mental picture of the phenomena. The cause of the precipitation in the experiments using small amounts of alcohol and other narcotics in the presence of electrolytes has been studied by Freundlich and Rona.[2] The researches of Kruyt and van Duin[3] have shown that a very pronounced influence on the coagulation of a sol can be brought about by capillary-active materials such as: amyl alcohol, phenol, etc., although these substances in the same concentration when alone do not coagulate the sol. Such capillary-active materials behave as sensitizers, that is they make the sols flocculate much easier. The analysis of this phenomenon is taken up in the reverse order relative to its occurrence in the cell. This is due to the fact that the experiments in the laboratory were carried out by treating the electrolyte-free sols with the organic material and examining the effect produced; then adding the electrolyte and studying the flocculation. The explanation that is given by Freundlich and Rona is that the capillary-active material will be adsorbed on the micellae in proportion to their capillary activity as Traube's work showed. The solution of the organic material was treated with the colloid and filtered. Then, by determining the concentration of the capillary material in the filtrate, the authors were able to show that the colloid adsorbed the substance. The concentrations were determined with the stalagmometer. The capillary active materials used in these experiments were: phenyl thiourea, camphor, thymol, tributyrin, methyl urethane, ethyl urethane, propyl urethane, and amyl urethane. The adsorption of this material will lower the charge on the particles, for the dielectric constant is lowered considerably. The dielectric constant of organic material is low relative to that of water; for the materials in the above it ranged from 5 to 20 while that of water is 81. This point is clearer if we assume that the charge on the particle is made up of two layers of ions, each layer containing ions of the same sign. In effect the arrangement is similar to that of a small condenser, the charge being a function of the distance between the layers and the dielectric constant of the medium that separates them. That the charge on the particles was actually decreased was proved by measuring the cataphoretic migration velocity. Now, since the charge is lowered, it is much easier to flocculate the colloid by small amounts of electrolytes. So that a sol that was once stable in the presence of low concentrations of electrolytes now becomes so sensitive that it precipitates. In the living cell this mechanism is reversed. The electrolytes are already present and have the colloids in a critical state; the addition of the narcotic brings about the flocculation. Laboratory experiments show that either method of addition will result in the same change and the explanation is the same for both cases. This process is thought to be quite general in relation to the colloids of the living cell and its application to other systems in the body will be pointed out later.

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[1] Physiol. Rev., **10**, 171 (1930).

[2] Biochem. Z., **81**, 87 (1917).

[3] Kolloidchem. Beihefte, **5**, 269 (1914).

As this phase of the coagulation is progressing, the colloidal systems of the cell or tissue have become so drastically altered that the material may no longer be considered normal. Most of the reactions of the cell probably take place on the surface of the colloids that are present. As the adsorption of the narcotic increases, much of the material will be displaced as in an exchange adsorption. Then as the charge on the colloids becomes less, the particles are not so able to retain polar compounds of the opposite charge. Then if the micellae begin to coalesce, the active surface is decreased. Finally, the stage is reached where the ions can neutralize the charge on the colloids effectively. The adsorption of compounds in the cell will now be very low and consequently the chemical changes of the living cell will be at a very low ebb. This mechanism applies not only to the proteins that constitute the protoplasm but to other bio-colloids such as enzymes, etc.

Indeed Verworn[1] has shown that narcosis is equivalent to the asphyxiation of the tissues. Independent confirmation of such work is so extensive that it is impossible to consider more than a few examples here. Much of the older literature is reviewed by Warburg and Wiesel[2] and Battelli and Stern.[3] Warburg and his co-workers[2] have made extensive studies on the oxygen consumption during narcosis and finds that the variation runs parallel to narcosis. Furthermore, this property of the narcotic did not depend so much on the chemical constitution but rather on the physical properties as one would predict from the work of Meyer and Overton, and Traube. The concentrations of a few of the narcotics required to reduce the oxidation velocity in Vibrio Metschnikoff 30-70% below normal is given in Table VII.

If the organisms were washed, or the narcotic otherwise removed, the oxidation velocity increased to normal, showing that the effect is quite reversible. Warburg has extended this work to other tissues.[4] He has

[1] "Narkose" (1912).
[2] Arch. ges. Physiol. (Pflüger's), **144**, 465 (1912).
[3] Biochem. Z., **52**, 226, 253 (1913).
[4] Z. physiol. Chem., **66**, 305; **69**, 452 (1910); **70**, 413; **71**, 479(1911).

TABLE VII

Substance	Concentration	Substance	Concentration
Methyl urethane	670 Millimols	Phenyl urethane	33 Millimols
Ethyl urethane	400 " "	Diethyl urea	170 " "
Propyl urethane	97 " "	Phenyl urea	18 " "
Butyl urethane	43 " "		

shown that in the case of yeast the same order of concentration of narcotics that were physiologically active in the living cell would also flocculate the colloids of yeast "in vitro." O. Meyerhof[1] showed that the mechanism involved in this coagulation was that outlined by Freundlich and Rona.[2] The yeast colloids were freed from electrolytes by ultrafiltration. When such colloids were treated with narcotics, there was no coagulation. If some of the filtrate was added to the system the material immediately flocculated. Then to show that it was only the electrolytes that caused this he evaporated the filtrate and burnt the residue to an ash. The ash when dissolved and added caused the same effect. In fact other electrolytes would bring about this flocculation also. It will be noticed that here again the mechanism is tested in the reverse order to which it occurs in the cells. In reality the electrolytes have the colloids in the critical state and the narcotic is responsible for the flocculation that is produced.

Battelli and Stern[3] in a very comprehensive extension of the work showed that narcotics inhibit oxidation in the liver and muscles. They isolated the nucleo-protein of the liver and showed that this inhibition ran parallel to the flocculation of the nucleo-protein "in vitro." Winterstein[4] and others showed that this depression of activity in the cells is an effect of narcosis and not the cause.

It is known, however, that there are exceptions to this general reaction. In some cases oxidation is increased and in others it is lowered and in still others narcosis has no pronounced effect on the oxygen metabolism. The reasons for these exceptions become apparent when we consider the nature of the oxygen metabolism.

It is well known that the energy required for the various purposes of the organism is obtained, except in special cases, entirely from oxidation. The high consumption of oxygen by muscle cells doing external work is clear, as also where glands are doing osmotic work. In discussions of this nature it must be kept in mind that the oxidation of one substance is always accompanied by the reduction of another. If an arbitrary zero oxidation potential is not defined, then there is confusion in the interpretation of the results. Assume that the zero is that of the atmospheric oxygen. In compounds whose oxygen potential is higher than that of atmospheric oxygen the region will be a place of reduction. But with compounds whose potential is less than that of atmospheric oxygen the same region will behave as a place of oxidation.

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[1] Biochem. Z., **86**, 325 (1918).

[2] Biochem. Z., **81**, 87 (1917).

[3] Biochem. Z., **52**, 226, 253 (1913).

[4] "Die Narkose" (1919).

Another phase of oxygen metabolism, in certain cases, is to oxidize toxic compounds to other substances that may be readily eliminated. There are many other ways of doing both of these things without oxygen. Now consider the case of a resting cell where the bulk of the oxygen consumption is utilized for the destruction of easily oxidized toxic compounds. Alcohol is a good example. If a small amount more of the substance is added to such a cell there is no reason why the oxygen metabolism should not increase. If the addition of the narcotic is faster then the cell can remove it by oxidation, or otherwise, then narcosis will be brought about and the oxygen consumption lowered. This is the general case. Lauren[1] noticed it in the germs of different plants, Elfving[2] in pea seeds, Markovine[3] in bean leaves, Kosinski[4] in Aspergillus niger, and Zaleski[5] in gladiolus bulbs that an increase in carbon dioxide production occurred when the plant tissues exposed to low concentrations of narcotics and a decrease in higher concentrations. Gerber,[6] Irving[7] and Johannsen[8] were drawn to the same conclusions.

Tashiro and Adams,[9] in their study on the nerves of the crab, *Libinia Caniculata*, found that weak concentration of chloral hydrate and ethyl urethane increased the carbon dioxide output; but, during narcosis by these narcotics, the production was greatly decreased. Baer and Meyerstein[10] studied this effect in the liver and Lussana and Roli[11] examined the effect in other tissues.

If oxygen is not used in some stage of the detoxication process then the narcotic will progressively decrease the oxygen consumption during the time the cell is undergoing narcosis. In this case it means that the cell is detoxicating the compound by some other means such as conjugation with substances in the cell as glycine, cystein, glutamine, ornithine, or glycuronic acid; sulphonation, methylation, hydrolysis, deaminization, etc. In many cases more than one of these methods is used on the same compound in successive steps such as hydrolysis followed by oxidation, etc. Another possibility is that the narcotic is diffusing into the blood stream and is being removed by some other organ such as the liver. Detoxication by means other than oxidation is of necessity employed by anerobic forms of life. It is well known that all compounds are not eliminated in the same way; one mechanism may be employed for a certain compound, while an entirely different method may be used on another substance in the same cell. The experiment of Winterstein[1] in which ethyl alcohol increased the oxygen consumption and ethyl urethane brought about a decrease illustrates the point.

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[1] Reference in Bot. Jahrb., **20**, 92 (1892).

[2] Ofversigt of Finska Vetensk. Societet, Forhandl., **28**, 36 (1885-86).

[3] Rev. gén. botan., **13**, (1901).

[4] Jahr. wiss. Botan., **37**, 137 (1902).

[5] Botan. Centr., **95**, 251(1904).

[6] Compt. rend. soc. biol., **54**, 1497 (1902).

[7] Ann. Botany, **25**, (2) 1077 (1911).

[8] Naturwiss. Wochenschr., **18**, 97, 109 (1902).

[9] Intern. Z. physik. Chem. Biol., **1**, 405 (1914).

[10] Arch. exp. Path. Pharmakol., **63**, 441 (1909).

[11] Boll. Sci. Bologna (8), **9** (1909).

Another phase must be considered, the enzyme systems may not be incorporated on the colloids of the protoplasm. If they exist as separate systems in the cell, then we have no assurance that a concentration of narcotic sufficient to flocculate the protoplasmic colloids will also flocculate the enzyme colloids to the same degree. The enzyme systems may be more or less sensitive to the narcotic than the other systems so that in such cells the decrease in oxygen consumption will not be necessarily parallel to the extent of narcosis.

All of the above data can be explained just as well from this point of view. As a matter of fact, it is believed that this is the more general of the two cases for it also explains the increased activities of other systems. It is a recognized fact among careful workers that many systems, other than the oxidizing one referred to above, show exactly the same phenomenon. This, in effect, amounts to the stimulating action of narcotics, when they are in low concentrations. For the purpose of discussion it is desirable to divide the stimulating effect into two divisions, one deals with the stimulation of growth, chemical reactions, etc., and the other with the increased irritability of protoplasm.

There is a great mass of data on the first division of the subject, but unfortunately no one has offered an adequate explanation. Nevertheless, the facts in the case are so numerous that they have been stated as a law, sometimes referred to as the Arndt-Schulz law.

The explanation offered above for the increased oxygen metabolism is believed not to be very general. This is due to the fact that it does not explain a case where the oxygen consumption is greater than enough to oxidize the toxic compound. If such data can be produced in future research to show this point it will settle the question. Up to the present time no such data have been found, so it was desirable to include this point in the discussion. At any rate such a mechanism would unquestionably play a minor rôle in a few cases.

As examples of this stimulating action on growth, chemical reactions, etc., Fokker[2] found that chloroform in low concentrations would stimulate the growth and activities of bacteria. Kochmann[3] mentions that ether in low concentrations stimulates the enzymatic processes of yeast. O. Nasse[4] found that curare stimulated many enzymes. If the normal action be given the arbitrary value of 100 then for invertase 100:249, ptyalin 100:124, and for pancreas ferment 100:119. The same author found that strychnine would inhibit the hydrolysis of proteins by pepsin but stimulated ptyalin 100:109. This effect of stimulation is completely abolished if the narcotic is allowed to act in higher concentrations; but, as the concentration is increased, the enzymes, as a general rule, are not affected as rapidly as the other substrates.

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[1] Biochem. Z., **61**, 81 (1914).

[2] Ned. Tijdschr. v. Geneesk., **1**, 168 (1891).

[3] "Handbuch exp. Pharm.," **1**, 221.

[4] Arch. ges. Physiol. (Pflüger's), **11**, 138 (1879).

It is this fact that allows us to add toluene, chloroform, etc., to enzymatic digestion experiments to prevent the growth of micro-organisms while not materially affecting the activities of the enzyme.

Now consider the theoretical case of a cell the enzymes of which behave in this manner, that is they are slightly less sensitive than the other colloids. The speed of the chemical reactions will be dependent upon the concentration of the reaction substances for the enzyme is only a catalyst. The amount of enzyme present will also govern the speed of the reaction; but, since the amount is constant, this effect may be neglected. The materials that are undergoing the reaction are adsorbed upon the many different colloidal substrates and are in equilibrium with a small amount of the substance that is in true solution. This amount in solution is the "effective concentration" as far as the speed of the reaction is concerned. Now as the narcotic is added to such a system, and the enzymes are less affected than the other bio-colloids, the narcotic will be first adsorbed upon these colloids in preference to the enzymes and will displace some of the reacting material from the surface of these inactive substrates. This amounts to an increase in their effective concentrations; hence the speed of the reaction will be greater. As more narcotic is added, the surfaces that were first affected become saturated and eventually narcotic reaches the concentration where it is adsorbed upon the enzyme, thus inhibiting its reactivity. As a general case this concentration is about the concentration at which the sensitive colloids have flocculated and the cell is already in a state of narcosis.

In this argument the concentration of the enzyme was taken to be constant. Assume a theoretical case in which the concentration of the narcotic that is stimulating is held constant and the amount of enzyme varied. We should predict from the above hypothesis that as the amount of enzyme was decreased the amount of adsorption per unit weight of enzyme would be greater, thus the inhibition of its activity would be greater. If the concentration of enzyme was increased, then the adsorption per unit weight of enzyme would be less and consequently the inhibition less. This case has been studied by Kaufmann.[1] He found in a digestion experiment with trypsin that a given concentration of chloroform had no effect, or was not harmful, when the concentration of chloroform had no effect, or was not harmful, when the concentration was 0.2% trypsin (Grübler). If only 0.1% was present the digestion was somewhat slowed; at a concentration of 0.08% enzyme the reaction was partially inhibited and at 0.02% completely inhibited.

R. Boehm[2] has also observed a very interesting phenomenon. Nasse[3] found that curare stimulated invertase in the ratio of 100:249. R. Boehm discovered that if the invertase was highly purified, that is if the bulk of the excess colloids were removed, the effect of the curare was practically nil. This is in line with the hypothesis and is what we would predict.

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[1] Z. physiol. Chem., **39**, 444 (1903).

[2] Boehm: Unpublished work.

[3] Arch. ges. Physiol. (Pflüger's), **11**, 138 (1879).

This suggestion of the possible mechanism is not stated as a strict law nor is further proof offered for its validity. It does explain the facts, it is simple, and since no one has offered a rational explanation of the phenomenon, it serves as a useful working hypothesis. The difficulty of the situation is that at the present time there are not enough of the necessary data at hand to unravel the problem completely and give a rigid proof.

The second division of the phenomena of stimulation, that is the increase in irritability, has been known for some time. Since it does not fit in with the scheme of other theories, it is often neglected and regarded as something that is "vital" and not to be explained in the usual manner. Nevertheless, protoplasm in the general case can be stimulated by narcotics, that is the movements of the organism are increased, certain nerves may be made more sensitive to stimuli, different organs and glands show a greater than normal amount of activity, etc.

As an instance of this, Nagai[1] found that the movements of amoeba were increased; also the ciliated epithelial cells of both higher and lower animals are found to be more active in the presence of a small amount of ether.[2] Balser[3] found that dilute alcohol favored the growth of certain bacteria. There are a great number of examples of this increase in irritability. Schurmayer[4] found that the movements of infusoria were easily made violent by dilute cocaine solutions and Alms[5] noticed the analogous increase in irritability of nerve endings when treated with cocaine solutions. Joachimoglu[6] discusses many other cases.

The explanation of this is that, when the protoplasm is completely coagulated or peptized, the organism is in a low state of activity; it is only when the protoplasm is on the border line of flocculation and peptization that the phenomena of irritability become pronounced. In the flocculation of the biocolloids by the narcotic the approach to this border line can be made very gradual So that at the critical state the phenomena of irritability can be made more pronounced, because one is able to approach nearer to the critical state. Since this is also the approximate concentration at which the enzymes are stimulated the phenomena are quite marked in some cases.

The question then arises as to the status of a stimulant. Can stimulants in higher concentrations behave as narcotics? There is some evidence that this is the case. If stimulants affect the nervous substrates, then there is no reason why they should not behave as narcotics in higher concentrations. Whereas, if they affect some less obvious substrate, in higher concentrations, they will narcotize only this system; so in some circumstances it will not appear to be acting as a general narcotic, because by narcosis one generally thinks of the narcosis of the nervous system.

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[1] Z. allgem. Physiol., **6**, 195 (1907).

[2] Engelmann-Hermann: "Handbuch der Physiologie," **1**, (1879); Lillie: Am. J. Physiol., **24**, 14 (1909); **29**, 372 (1912); Nerlich: Inaug.-Diss., Halle (1920).

[3] Inaug-Diss., Giessen (1914).

[4] Jena. Z. Naturw., **24**, 438 (1890).

[5] Arch. Anat. Physiol. Abt., **1888**, 416.

[6] Biochem. Z., **156**, 224 (1925).

Caffein is classed as a stimulant and is not usually considered as a narcotic but when applied directly in higher concentrations to nerves it behaves exactly like a narcotic.[1]

Also strychnine, which will be discussed in detail later, has been found to be a very potent narcotic despite its classification as a stimulant. Strychnine frequently interferes with the oxygen metabolism and the toxic effect appears before the narcosis, so this result is not well known. Nevertheless, when proper provisions are made to correct for this it leads to a very pronounced narcosis. Theoretically, it might be possible to find compounds that would be so weakly adsorbed that in higher concentrations they were not quite able to flocculate the colloids and thus be a pure stimulant but such compounds have not yet been found.

The converse of the above question, whether all narcotics will behave as stimulants can also be answered. They should all show this phenomenon, although the stage of excitability may be passed over so rapidly that it will not be pronounced and consequently be overlooked.

Indeed this must be a very perplexing state of affairs to that large group of research workers who attempt to relate physiological action to chemical constitution. The chemical constitution of drugs is independent of concentrations, so this change in physiological action can only be interpreted from the point of view of the physical or colloidal state. The constitution of a compound will determine its physical properties such as solubility, etc., and indicate certain substrates in the body upon which it will be adsorbed but it does not indicate the mechanism by which it becomes effective. This effect of concentration is not confined to that group of compounds classed as narcotics or stimulants. Saccharine, for example, is very sweet only when dilute, higher concentrations seem to paralyze the sense of taste for it. Then again the well-known effect of dilution on perfumes. A perfume may have a very pleasant odor when dilute but in higher concentrations the odor is drastically altered and often weaker. The blending of perfumes is as much a problem of concentrations as the actual combination of several essences.

The experiments of Binz, Claude Bernard, and others have offered good evidence that reversible coagulation actually does take place within the living cell. However, one would like to make the experiments more convincing, first proving that coagulation does occur in the normal cell and secondly, that this coagulation is reversible. The most convincing manner in which this could be proved would be to examine the colloids of a cell under the ultramicroscope and observe what takes place. Then, in order that the cell be perfectly normal we can take some unicellular organism in its normal environment. This has the added advantage of being not only simple but that we are able to examine all the organism at the same time, thus seeing a complete picture of the mechanism of narcosis.

Also, if the narcotic is removed we shall be able to see whether the coagulated material is peptized or not. This important point then will not depend upon indirect evidence. Such an experiment would be independent of theories and hypotheses and it would show directly whether coagulation occurred and whether it was reversible.

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[1] 'Handbuch exp. Pharm.," 2, 527.

This interesting experiment was carried out, using ordinary baker's yeast as the living cells. Young, vigorous cultures were prepared by inoculating yeast into Laurent's medium made up with 1.5% dextrose. Subcultures were made every twenty four hours, the third subculture being used in the experiments. A portion of the culture was then placed under the ultramicroscope and the normal state of the colloids observed. The colloidal material is easily visible and the Brownian movement is pronounced. In some cells small vacuoles can be seen. Sometimes one is able to see a few dead cells, these are easy to identify for all the material within then is completely coagulated. A photograph was then taken to make a permanent record and is reproduced in Fig. 1.

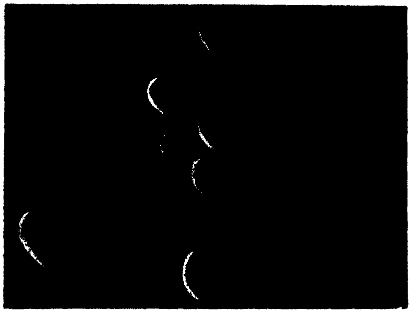

FIG. 1
Normal yeast cells

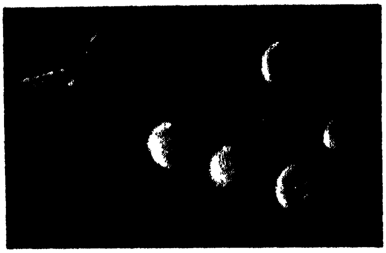

FIG. 2
Narcotized yeast cells

The culture was then treated with the narcotizing concentration of amyl alcohol, about 2% and again placed under the ultramicroscope. At first nothing happens, after about ten minutes the Brownian movement is noticed to be decreased and a few minutes later small aggregates of colloids are seen. The coagulation now goes much faster and in a few minutes a light but very pronounced flocculation occurs. The complete change usually requires about twenty-five minutes, although, the time naturally depends upon the concentration of the narcotic, the temperature, and the individual culture. This same experiment was then tried with such other narcotics as chloroform, paraldehyde, ether, and chloral hydrate. The result in all cases was the same —coagulation. Thus the first postulate of the theory is shown to be an actual fact. A photograph of this change was then made and is reproduced in Fig. 2.

The narcotized culture was then placed in a centrifuge and the cells thrown down. The supernatant liquid was poured off and fresh sterile medium added. The cells were washed in this way twice and again examined under the ultramicroscope. The material in the cells is still coagulated but in a few minutes a very slight Brownian movement within the cells can be seen. The aggregates break up into smaller particles and the motion becomes more pronounced.

At the end of twenty-five or thirty minutes the material is completely peptized and the cell is normal in every respect. The yeast will ferment the media and reproduce just like the normal cells. Thus it is shown that the second postulate is a fact. However, this recovery does not always follow. If the narcotic has acted in high concentrations or for a too great a length of time the material cannot be peptized again. This merely shows the toxic effect of an excess of the narcotic.

FIG. 3
Spinal ganglion cell of dog, not narcotized (Marinesco).

FIG. 4
Spinal ganglion cell of dog, narcotized (Marinesco).

It was desired to try an electrolyte of higher valence and it was found that cerium chloride in a dilution of 1-3000 was not injurious to yeast cells.[1] The experiment was carried out exactly as described above and it was observed that the flocculation occurs much faster but is otherwise the same. When such cells are washed with media free from cerium chloride and narcotizing agent the peptization is also much faster being almost complete in ten or fifteen minutes.

The researches by Professor F. Marinesco[2] on the colloidal structure of living nerve cells has dispelled such erroneous conceptions as neurofibrils and Nissl bodies; that can be seen only in fixed and properly stained preparations. His experiments involved the direct observation of the colloids of the nerve cells under the ultramicroscope. These careful experiments also give positive evidence that this same sort of coagulation occurs in the living nerve cell. Fig. 3 is a reproduction of one of his photographs of the colloids in a spinal ganglion cell of a young dog. This may be considered as the normal appearance it would present if it could be observed in the body. The only aliphatic narcotic that he studied was ethyl alcohol. Fig. 4 is a reproduction of a photograph of the nerve cells after treatment with dilute alcohol.

The coagulation is seen to occur not throughout the whole cell but only in a small portion of the nucleus. The extranuclear material is unchanged, showing the specificity of the adsorption of alcohol upon the different substrates of the same cell. Marinesco made no experiments to determine the reversibility of the coagulation; but, since we know that reversibility is possible, this point is not now important.

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[1] Arch. exp. Path. Pharmakol., **100**, 226 (1924).

[2] Kolloid-Z., **11**, 207 (1912); III^{e} Congrès internationale de Neurologie et de Psychiatrie, Gand, 20-26 (1913).

As pointed out in the first postulate, this reversibility exists as an independent fact, and whether our speculations as to the cause are right or wrong it will not change the status of the theory. The recovery depends upon the peptization of the flocculated material in the cell. Peptization may be regarded as the reverse of coagulation and can usually be accomplished in the laboratory by one of three ways. In some cases it can be effected by adding an ion that is adsorbed and thus raising the potential difference between the particle and the solution. In other cases the removal of the coagulating ion by washing is sufficient; an example of this is the peptization of arsenious sulfide by washing. Another method depends upon the adsorption of a different colloid. The peptization in the cell is in all probability brought about by the removal of the narcotic and peptization by the electrolytes.

The removal of the narcotic can be accomplished in two ways; by diffusing into the surrounding blood or lymph and being later destroyed in some other part of the body, and removal by chemical destruction within the cell. Both of these factors contribute to the elimination. It is recalled, that in attempting to remove an adsorbed substance from a substrate by washing it is extremely difficult to remove the last traces. Within the cell this elimination is facilitated by the fact that chemical reactions are occurring on the surface of the colloids and consequently the removal is much faster than if it were being accomplished by physical means alone.

Since the peptization of the agglomerates depends upon the adsorption of the ions within the cell another factor is introduced. The coagulation may be of two types. If the particles have just had their charge lowered to the point of instability they flocculate without much change in surface. On the other hand, if the narcotic is concentrated enough so that after flocculation the lowering of the surface tension will permit the aggregates to coalesce, then the active surface is much less. The material is in larger aggregates and appears granular. Since this is responsible for the slow peptization it is also responsible for the toxic action. It is easy to distinguish between the two types of coagulation when the material is examined under the ultramicroscope. Figs. 5 and 6 are reproductions of two photographs of Marinesco showing the toxic effect of zinc sulphate and of hydrochloric acid on the nerve cell. Compare these with Fig. 4.

Winterstein and others are quite right in insisting that coagulation is responsible for the toxic action; they are wrong in assuming that all coagulations are irreversible.

In this connection it is interesting to note that disinfectants such as mercuric chloride produce this type of coagulation. If the disinfectant is in low concentrations then it behaves similar to the narcotics. First it stimulates the growth and activities of the organism upon which it is acting, then in slightly higher concentrations it inhibits their growth but does not kill them. Under certain conditions mercuric chloride will produce a reversible coagulation[1] and thus behaves as a narcotic.

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[1] Arch. Hyg., 89, No. 8, (1920); 93, 252 (1923); Münch. med. Wochenschr., 67, 1166 (1920).

However the manner of elimination, the film of narcotic is replaced by water and the peptizing agents originally displaced by the narcotic. Provided that the coagulation is not extensive and granular, on complete removal of the narcotic the cell again returns to normal. Since there are several independent colloidal systems within the cell with specific functions, these may not recover at the same rate. However, if these systems recover at the same relative rate and in the same order in which they were narcotized *the cell should pass back over in the reverse order the phenomena it exhibited when undergoing narcosis.* It is recalled that narcosis is preceded by a stage of excitability; on recovery the normal state should be preceded by this stage of increased irritability.

FIG. 5
Coagulation by zinc sulphate (Marinesco).

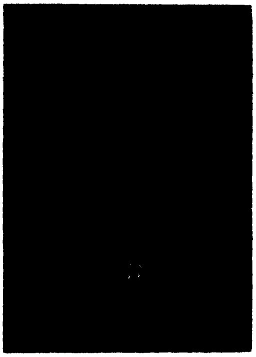

FIG. 6
Coagulation by hydrochloric acid (Marinesco)

This is usually described as the "after effect" of the narcotic; that is, the subject is more reactive to smaller stimuli than usual. Gwathmey's "Anesthesia" gives an excellent description of the after effect of ether narcosis: "It has been stated that if ether is administered according to modern methods, with the utilization of preliminary and accompanying factors, the subject emerges, as a rule, from the anesthetic state as if from normal sleep, feeling no ill effects so far as the anesthetic is concerned. Under circumstances, however, even with the most careful technique, the recovery period may be marked by retching, nausea, and vomiting. . . . Transient mental disturbances, amounting in some cases to mania and dementia, have been reported. Muscular excitement may be noted for a brief period, and in rare instances coreiform movements have been known to last for two or three weeks." Hiccoughs, vomiting, retching, choreoid movements, general uneasiness, etc., are symptoms of this increased irritability. Often these are not very pronounced and are overlooked. If they are marked, the tendency seems to be to describe the patient as "abnormal" or "neurotic and hysterical."

To obtain a more exact view of this prediction a case should be taken where "hysterical symptoms" are excluded and use a drug that is both a powerful stimulant and a potent narcotic. Strychnine shows both of these properties and one could not interpret the tetanic spasms produced in frogs as being due to hysteria or abnormality. One would predict in this case that, if the recovery of the colloidal systems is in the same order, the animal will go back through the tetanic stage after narcosis before returning to normal. This very thing has been known for a long time; but its explanation and relation to narcosis has not been clear. It has been noted that small doses of strychnine will produce violent tetanic spasms in human beings, and larger doses will produce death. In frogs the same thing occurs except that the death is only apparent when the concentrations are not too great. First after the injection the tetanic spasms occur, the time of appearance depending upon the animal used, then these slowly decrease in intensity and finally the animal loses all response to stimulation and is in a deep narcosis. The narcosis is very pronounced and may last for several days, nearly the only sign of life being a very weak heart action. If the frog is placed in fresh water frequently, to aid the elimination, the animal recovers and goes back through the violent tetanic spasms again. This may be for a much longer time than the original spasms, for the elimination is not rapid. Vulpian[1] noted that this second period of tetanus often extended over a period of time up to thirty days.

E. Poulsson[2] describes the phenomena in relation to Esculenta. The first day of the experiment 5 mgs. of strychnine nitrate were injected subcutaneously; the animal was paralyzed ten minutes later. From the second to the sixth day complete paralysis. On the seventh day there appeared weak breathing movements and barely noticeable fibrillar contractions. During the eighth and ninth days the attacks of convulsions became more frequent. From the tenth through the sixteenth day the animal was in complete tetanus. The animal died on the seventeenth day in convulsions. This is an exaggerated picture of narcosis and the recovery, but, nevertheless, the simplicity of the experiment and the overemphasis of the phenomena illustrate the point in question.

The next question one is interested in is: if strychnine is such a good narcotic why does death occur in human beings before narcosis is produced? It is known that in cases of death due to strychnine poisoning the person is conscious up to the time of death. Pharmacologists have already investigated this problem and found that death is due to other causes than the direct toxicity of the strychnine. For instance, strychnine brings about profound disturbances in the transmission of oxygen by the blood. Harley[3] analyzed samples of blood treated with strychnine and found in one case, with calf's blood, that the ability to yield up oxygen was greatly decreased. The hypothesis at that time was that the poisoning was due to asphyxiation. Richter[4] and W. Lerab[5] showed that artificial respiration with oxygen would decrease the toxic effects tremendously. Although this fact is well known there are many other interpretations. Rosenthal,[6] Brown-Sequard,[7] Filehne,[8] Ananoff,[9]

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[1] "Leçons sur l'action physiol. des substances toxiques," (1882).
[2] "Handbuch exp. Pharm.," **2** (1), 341.
[3] Lancet, **1**, 619, 647 (1855).
[4] Z. rat. Med., 76 (1863); Göttinger. Anz., **1862**, 165.
[5] Arch. Anat. Physiol., **29** (1867).
[6] Compt. rend., **64**, 1142 (1867).
[7] Arch. Physiol., **4**, 204 (1870).
[8] Arch. Anat. Physiol., **1873**, 361.
[9] Centr. med. Wiss., **1874**, 417.

Gies and Meltzer,[1] have all made important contributions to the explanation of this effect. This phase is more of a physiological than a colloidal problem so no attempt will be made to cover it here.

It was mentioned above in connection with the work of Alms,[2] that cocaine increased the irritability of nerve endings. This effect is also pronounced in the recovery. In fact it is so marked that cocaine is not used on areas which are to be cauterized for as the effects of the cocaine wear off the pain becomes greater than normal.

This effect will be noticed with most narcotics though the stage may be passed over so rapidly that little or no inconvenience will be experienced. On the other hand if the drug is eliminated slowly, as in the case of strychnine, the effect is very marked. Thus, there are two ways to keep this effect at a minimum; avoid an overdose so that there will be less to eliminate and secondly hasten the elimination.

We can see that this increased irritability is not desirable as far as the medical practice is concerned. There is one interesting way in which recovery from this phase can be made very rapid. As mentioned above the adsorption of narcotics is specific; but the common inhalation narcotics, in general, are extensively adsorbed by all tissues. Now if a large field of such tissue could be removed from the circulation and thus could not adsorb the narcotic the recovery could be made very rapid. For in the first place less anesthetic would be required. Then when the tissue is thrown back into circulation again it would literally "blot up" the narcotic until the concentration was at a lower level than the excitatory concentration.

Corning[3] did this experiment by cording the thighs of an individual, so as to interrupt both the arterial and venous circulation. The tissue below this area was then entirely free from the narcotic. He cites an example of a case in which it required six-seven minutes to anesthetize a patient but by cording the thigh and cutting off "one third of the man" the patient was anesthetized in three minutes. After the operation the ligatures were removed and the patient recovered from the effect of the anesthetic instantly.

This rapid recovery depends upon the general adsorption of the narcotic and will not be noticeable in cases where the narcotic is specifically adsorbed by small amounts of tissues, for example the nerves, for the extra tissue used as an adsorbent is not great enough to make a decided difference in the concentration when thrown back in circulation.

This can be at the most only a superficial survey of the mechanism of narcosis but since we are interested in the theory as much as in the mechanism perhaps it would be well to look for confirmation of the theory on other grounds. It may have already been noticed that in this theory there is no mention of the manner in which the coagulation is brought about. That is, if this change could be brought about by physical means the result should be the same. There is evidence that this is the case.

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[1] Am. J. Physiol., **9**, 1 (1903); Berl. klin. Wochenschr., 1776 (1910).

[2] Arch. Anat. Physiol., **1888**, 416.

[3] N. Y. Med. J., Oct. **1887**, 22.

Theoretically there is another manner in which agglomeration is possible. Consider a case in which the stabilizing ions are not strongly adsorbed. If such a system is treated with water the concentration of the ions will be decreased and their adsorption lowered. If this is extended the charge on the colloids can be cut down to a value such that the particles are no longer stable and flocculate. Anyone who has purified sols by dialysis is familiar with the fact. So here is a case where water can act as a narcotic and any explanation based upon distribution coefficients, membrane permeability, or loss of water is doubtful. Such states as this may not be well known but they are not uncommon. Wyeth[1] has studied the use of water as a local anesthetic. At one time water was used in dentistry and certain minor surgical cases. Heilbrunn[2] found that in the case of sea-urchin eggs the protoplasm could be coagulated by distilled water, or diluted sea water, and that this effect was reversible if not carried too far. This method of local anesthesia has not found favor due to the fact that the injections of large amounts of water causes mechanical damage to the tissues and is painful. This type of local anesthesia has been called "anesthesia dolorosa" by Liebreich.

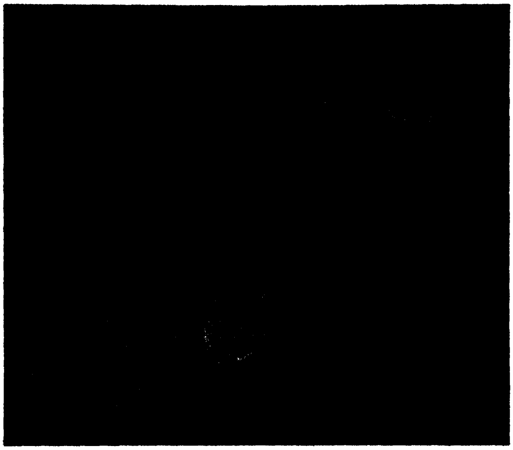

FIG. 7
Action of water on the nerve cell (Marinesco).

Fortunately, Marinesco has investigated the effects of water upon the nerve cell and the data support the theory that coagulation is produced. Fig. 7 is a reproduction of his photograph showing this effect. No other theory of narcosis is able to account for this peculiar effect of water.

Heat is a physical phenomenon and has a very marked effect on protoplasm. The first effect of heat is to induce narcosis, that is the organism loses all response to stimulation. If the organism is removed to a lower temperature it recovers. Continued exposure or a higher elevation of the temperature will result in death. Heilbrunn[1] has shown that in the initial stages of heat treatment of the eggs of the sea-urchin and the clam *Cumingia* there is a reversible coagulation of the protoplasm. This is exactly what the theory would predict. This coagulation is not reversible if the eggs are kept at the coagulation temperature, 32°-33°, for too great a time. Furthermore, this coagulation precedes the death of the cells. There are other workers that have noticed the reversible coagulation of protoplasm by heat. Sachs[2] studied the phenomenon in relation to plants and Gotschlich[3] in the case of heat rigor in frog muscle. Heilbrunn finds that the effect of ether is similar to that produced by heat, in fact the effects are *additive*. If the eggs are first treated with ether they become more sensitive to heat; the reverse was not tried. Heat prostration in human beings may also be related to this type of phenomenon.

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[1] N. Y. Med. J., Jan. 6 (1906).

[2] Biol. Bull., 39, 307 (1920); Exp. Zool., 30, 211 (1920).

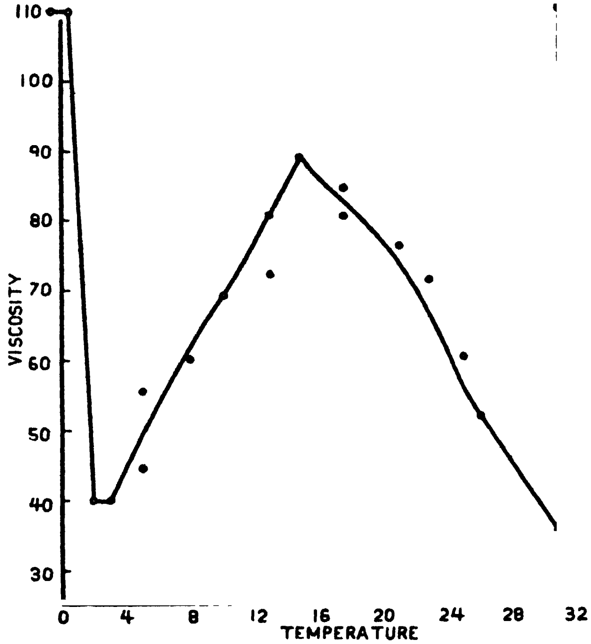

FIG. 8
Heat coagulation of protoplasm (Heilbrunn).

The effect of cold upon sensibility is probably more familiar. At the present time the production of local anesthesia by freezing with ethyl chloride is quite common. This is quire an old practice; an Italian surgeon, Severino and his pupil, Thomas Bartholinus, called attention to this effect of cold in the sixteenth century. Napoleon's surgeon, Larrey, in 1807 again called attention to the fact that amputations carried out on the battle fields at very low temperatures (1°-19°) were not painful. At the present time there is no direct evidence that coagulation does take place as one would predict on the basis of the colloidal theory; provided this phenomenon is a true narcosis. However, the extensive researches of Heilbrunn on the viscosity of protoplasm[1] give every indication that coagulation does occur. It is known that heat coagulates protoplasm and the viscosity changes during this coagulation are exactly like those produced by cooling. Fig. 8, which is the same as that on p. 109 by Heilbrunn, illustrates this point.

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[1] Am. J. Physiol., **69**, 190 (1924).
[2] Flora, **22**, 5 (1864).
[3] Arch. ges. Physiol. (Pflüger's), **54**, 109 (1893).

Heilbrunn is quite definite on this point[2]: "It was shown previously that in the *Cumingia* egg a marked increase in viscosity occurred at one degree above freezing. It is quite possible that such a coagulative effect would be an important factor in causing the death of cells at temperatures just above the freezing point of water. Mammalian muscle contracts on cooling to 5°[3]. There is thus a cold rigor as well as a heat rigor of muscle. In the *Cumingia* egg, the coagulation due to cold is reversible, just as is the heat coagulation. But it is not at all improbable that after a lengthy exposure to 1°C., the protoplasm may be permanently injured. Concerning the reasons for the sudden increase in viscosity at temperatures just above the freezing point, we have at present no real information. A few scattered observations show that in this case too there may be a change in the physical properties of the lipoids of the cell. In the *Cumingia* eggs centrifuged at 1°C., the lipoids present a very characteristic appearance, quite different from that found in similar cells at normal temperatures.

"Most animals and plants are killed by cold only when their temperatures drops below the freezing point of water. Owing to various economic phases of the subject, there have been many more studies of the cold death of plants than of animals. In temperate or cold climates, the death of plants as a result of exposure to cold is an important agricultural problem.

"The older literature on the effect of freezing temperatures on plants has been well summarized by Pfeffer.[4] For later summaries see Chandler,[5] Rosa,[6] Newton,[7] Doyle and Clinch,[8] and Akerman.[9] Generally speaking, death in plant cells depends on the formation of ice crystals. At one and the same temperature, death occurs if crystals of ice are formed, whereas if no crystals appear, the cells live on. The crystals may be formed either within the cells or outside of them. Concerning the cause of death, the leading theory is that of Müller-Thurgau.[10] This author holds that as ice forms, the salt concentration of the rest of the protoplasm increases until the death point is reached. Müller-Thurgau's theory is supported by Molisch[1] and by Maximow.[2] However, the latter author believes that in addition to the salt effect following ice formation, there is also a mechanical effect of the ice crystals on the colloids of the protoplasm. If the Müller-Thurgau theory is correct, then cold death at freezing temperatures is really a special case of the toxic action of high concentration of salt in the cell.

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[1] Protoplasma—Monographien, Vol. I.

[2] "Colloid Chemistry of Protoplasm," 123.

[3] XIth Intern. Physiol. Congress, Quart. J. Exp. Physiol., Supplement, 69 (1923).

[4] "Pflanzenphysiologie," (1904).

[5] Missouri Agr. Exp. Station Research Bull., No. 8 (1913).

[6] Missouri Agr. Exp. Station Research Bull., No. 48 (1921).

[7] J. Agr. Sci., **12**, 1 (1922).

[8] Sci. Proc. Roy. Dublin Soc., **18**, 219 (1926).

[9] "Veröffentlichungen der Knut und Alice Wallenberg Stiftung," No. 10 (1927).

[10] Landwirt. Jahrb., **9**, 133 (1880); **15**, 453 (1886).

There is still another kind of anesthesia that must be considered, that is electrical anesthesia. About the beginning of the twentieth century a number of workers discovered independently that electrical currents under certain conditions would produce narcosis. The subject has received quite a bit of publicity and is quite novel. Both general and local anesthesia can be produced by this method. The bulk of the work seems to be confined to the determination of the optimum conditions under which the effect can be best produced. When used under these conditions it could be employed in minor surgical operations to some advantage.

The method consists in placing two electrodes in such a position that the chosen part of the body or limb is included in the circuit. L. G. Robinovitch gives an excellent summary of the method and literature in "Anesthesia" by Gwathmey.

The most interesting thing of the whole situation is how can this effect be explained upon the older theories of narcosis. There is no relation between an electrical current and distribution coefficients nor could the effect be included in Kochmann's dehydration theory. On the colloidal theory one suggests that the current caused a slight flocculation of certain colloidal systems. It is known that the inorganic salts are, in part, responsible for the peptization or stability of the colloids in biological systems. Now if two electrodes are placed such that the cell is between them and a current passed, we know that the ions will migrate either to the anode or cathode depending upon their charge. Since the stabilizing concentration of these ions in the cell is very critical any small deviation will cause a flocculation. The case is similar to an electrical dialysis. When the current is disconnected the blood will enable a uniform distribution to take place and equilibrium is again established; this is responsible for the recovery.

The experimental researches of Heilbrunn[3] support this view. "Electric currents have a marked effect on various types of living material. In muscle and nerve physiology, the electric current is the most common means of stimulation. Lower forms of animal life and various plant tissues also show a characteristic response to the passage of electricity. It is to be expected, therefore, that the protoplasmic colloids should undergo changes following exposure to electric currents. There is an abundance of evidence to prove that this is the case

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[1] "Untersuchungen über das Erfrieren des Pflanzen" (1897).

[2] Jahrb. wiss. Botanik, 53, 327 (1914).

[3] "Colloid Chemistry of Protoplasm."

"In 1862 Brücke showed that electric currents produced a cessation of Brownian movement in the salivary corpuscles or leucocytes of human saliva.

"Kuhne[1] found that the passage of an electric current from an induction coil caused a cessation of Brownian movement in the protoplasm of the stamen hairs of *Tradescantia.* Chifflot and Gautier[2] also found that the passage of an electric current stopped the Brownian movement in the cells of the alga *Cosmarium.* Bayliss[3] studied the effect of currents from an induction coil on Brownian movement in the protoplasm of ameba. The amebae were placed on a slide in a drop of water, and the electrical current was led to the drop through strips of platnium foil. With this technique, there is of course the possibility that various chemical substances formed at the electrodes may have an effect on the protoplasm. But Bayliss' observations were usually made very rapidly, so that this was probably not a factor. In studying the Brownian movement, Bayliss used a Zeiss paraboloid condenser, and he focussed his attention on the ectoplasm of the pseudopodia. Here one can observe a very vigorous movement of granules invisible with bright field. On the passage of an electrical current, this movement "ceases almost instantly, as if the protoplasm had been frozen." Then when the current is stopped, the Brownian movement begins again. In order to obtain these results it is necessary to use currents that are neither too weak or too strong. The latter produce an irreversible coagulation of the protoplasm.

"From these studies on Brownian movements; it is apparent that electric currents can produce a reversible gelatination or coagulation of the protoplasm. A much more exact study of the effect of the electric current on the colloidal properties of protoplasm was made by Bersa and Weber.[4] These workers were careful to exclude any possible error due to the formation of chemical decomposition products at the electrodes. The current passed from carbon electrodes through troughs containing tap water, and then to the tissue by way of long strips of moist filter paper. Water and filter paper were changed from time to time, so that there was no possibility of the diffusion of chemicals from the electrodes to the cells. The material used was the stalk (epicotyl) of the bean plant *Phaseolus multiflorus,* and the current was passed through pieces of stalk about 1-2 cm. long. The viscosity of the protoplasm was determined by the centrifuge method. The results of the experiments are very clearly summarized by Bersa and Weber, and the account that follows is practically a translation of their words.

"In order to produce a viscosity increase in the protoplasm, an exposure of only $\frac{1}{4}$ to $\frac{1}{2}$ minute is necessary, if the current is relatively strong (5-10 milliamperes). With weaker currents (0.15-5 milliamperes), an exposure of 1 to 4 minutes is necessary to produce the same effect. The increase in viscosity produced by these currents is considerable, for it is at least a three-fold increase. The effect is reversible, and after a recovery period of 20 to 40 minutes, the viscosity becomes as low or nearly as low as it was before exposure to the electric current. The results of Bersa and Weber find confirmation in some experiments of Zeidler.[1]"

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[1] "Untersuchungen uber das Protoplasma und die Contractilitat" (1864).

[2] J. de Bot., 19, 40 (1905).

[3] Proc. Roy. Soc., 91B, 196 (1920).

[4] Ber. deutsch. botan. Ges., 40, 254 (1922).

While these physical methods may never enjoy the popularity of chemical narcosis, still they are important from a theoretical standpoint and must be taken into consideration. An important phase of the colloidal theory is that it is able to account for this data. It is impossible to explain these cases on the other theories.

A peculiar case of narcosis that finds no good explanation in other theories is that produced by magnesium salts. S. J. Meltzer[2] found that subcutaneous, intravenous or intraspinal injections of magnesium sulphate would produce narcosis. Meltzer pointed out, as secondary actions, undue prolongation of the paralysis and retention of the urine. However, these effects could be minimized by washing out the spinal canal with normal saline solution. Tucker[3] showed that solutions of magnesium sulphate could be used as a local anesthetic. Wiki[4] has extended the study and investigated the relation of concentration of the salt to strength of narcosis. Meltzer found that in certain cases the combination of magnesium salts and ether could be used to advantage. The injection of one cc of sterile 25% solution of magnesium sulphate per kgm. of animal into the femoral muscle brought about greater relaxation with smaller amounts of ether. The well known antagonism between calcium and magnesium salts suggested that calcium salts would greatly facilitate the recovery from the effects of the magnesium.

H. B. Weiser[5] has formulated clearly the colloidal mechanism of the antagonism of ions in biological systems, so it is not necessary to discuss the reason further in this place. Meltzer found that the injections of calcium salts would quickly remove the influence of the magnesium ion.

No attempt is made to review the literature on the subject but the brief outline just given showing the use of magnesium salts for spinal anesthesia justifies the opinion that this type of narcosis is no passing fancy. It does not depend upon some peculiar property of certain cells, for it is quite general; and the explanation must not be based upon any usual assumptions. Clearly, the theory of Meyer and Overton offers no explanation nor would this theory even predict that magnesium salts would behave in this manner, for the solubility of such salts in lipoids or fats is very low relative to the solubility in water. Neither does Traube's theory offer an explanation, the surface tension of a 23% solution of magnesium sulphate at 18° is 78. While that of water at the same temperature is 73. There is no lowering of the surface tension here, quite the contrary. To explain this phenomenon on the basis of the colloidal theory however, is quite simple. We only have to postulate that the magnesium ions will partially flocculate some one of the colloids in the part that is affected i.e. the nerve cell. This postulate is no idle assumption. Marinesco has studied the effect of magnesium sulphate on the spinal nerve cell and found that indeed the predicted flocculation occurred. Fig. 9 is a reproduction of his photograph showing this coagulation.

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[1] Botan. Archiv. 9, 157 (1925).

[2] Berlin klin. Wochenschr., Nr. 3, 73 (1906).

[3] Therap. Gaz., Nr. 5 (1907); Revista espec. medicas, Nr. 199. 475 (1907); Merk's Archives, Nr. 6, 178 (1907).

[4] Arch. Intern. Pharmacodynamie, 21, 415.

[5] J. Phys. Chem., 30, 20 (1926).

In the zone of flocculation in the extranuclear material one can still distinguish between the individual agglomerates of the coagulated material, thus, showing that this partial or "semicoagulation" is different from the normal coagulation or denaturation of proteins in that the material is not coagulated to such a point where the repeptization would be excessively slow, due to a marked decrease in the surface of the agglomerates. As was pointed out, such a state as this would be unfavorable to the recovery of the cell. Should such an extensive flocculation occur, then the cell could not be expected to recover and the agent that would bring about this condition would be classed as a toxic drug. It has been known for a long time that zinc sulphate could not be used in intraspinal injections due to its high toxicity. Fig. 5 shows the same type of ganglion cell after treatment with zinc sulphate. It is easy to see why one behaves as a narcotic and the other as a toxic agent. The flocculation of the colloids is quite marked and can be seen to be quite different from that produced by magnesium sulphate. The large close-packed agglomerates show definitely that repeptization of the colloids in these cells would be difficult.

FIG. 9
Coagulation by magnesium sulphate (Marinesco).

The case in which narcosis is produced by HCN or certain metallic cyanides is interesting, in that the amount required to bring about narcosis is so small that flocculation of the colloids seems excluded.

Dontas[1] found that concentrations of sodium cyanide of 0.005%. or less were narcotic for tadpoles, higher concentrations were so toxic that there was no recovery from the effect. At first sight this seems to exclude flocculation, for HCN, which is formed by the hydrolysis of the dilute solution, will not flocculate proteins in concentrations below 40%.[2]

The cyanide ion has a very marked effect on certain enzymes while other enzymes such as lipase, ptyalin, pepsin, and trypsin are not disturbed. However, such enzymes as catalase, platinum black and enzymes whose action depends upon the presence of metallic elements such as iron and copper are easily poisoned. Warburg's explanation[3] that the inhibition is due to the formation of complex ions may be wrong. For in some well-studied cases the phenomena are reversible, e.g., if the HCN is removed by blowing a stream of air through the solution; the enzyme is active again.[4] This seems to indicate that adsorption is more important, for the complex cyanide ions are relatively stable. This is also in line with the work of Dixon[1] in that there is no definite stoichiometrical relation between the concentration of the cyanide ion and the inhibition.

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[1] Arch. exp. Path. Pharmakol., 59, 430 (1908).
[2] Gaz. med. de Paris (35), 4, 675 (1849).
[3] "Handb. d. experim. Pharm.," 1, 703.
[4] Meyerhof: "Chemical Dynamics of Life Phenomena."

When a tissue is exposed to the cyanide ion there is an inhibition of the oxidation process, in higher animals this is shown by the fact that the amount of available oxygen is practically the same in both the venous and arterial blood, that is, the tissue has been unable to utilize the available oxygen. On lower animals the effect is similar to an atmosphere of hydrogen.[2]

As an explanation of the narcotic effect we may assume that the products that are normally oxidized will accumulate within the cells until their concentration is sufficient to flocculate the colloidal systems. Experiments on protoplasm bear out this point of view.[3] Protozoa were found to react in all physical appearances just as if they had been treated with quinine or morphine alkaloids. It was found that in many cases the protoplasm became swollen, this is probably due to the accumulation of the acidic products which cause the proteins to increase the degree of imbibition.

The conditions for recovery are not different from those of an ordinary narcotic, that are outlined in another part of this paper. The oxidation within the cell is not completely destroyed[4] but is lowered and the cell can regain its activity upon the removal of the CN ion if the dose has not been so great that irreparable damage has been done.

This paper suggests that the action of narcotics is due to a reversible coagulation of the bio-colloids. This effect, as already indicated, can be accomplished in two general ways: by direct coagulation due primarily to the narcotic, and secondly by indirect action, by interference with some normal function of the cell such that products are allowed to accumulate which will cause the coagulation.

The question was raised by A. P. Mathews[5] concerning the ability of nitrous oxide to flocculate bio-colloids. This question may be generalized by extending it to other physiologically active gases. There is no reason why gases should behave differently from solid and liquid narcotics, i.e., there exists the possibility of direct action, indirect action, or inertness depending upon the physical and chemical properties of the substance in question.

The recent introduction of ethylene oxide as a strong gaseous disinfectant[6] and its rapid action at low concentrations would suggest that this gas might coagulate bio-colloids directly. This was confirmed in the case of yeast by direct observation under the ultramicroscope. The gas was slowly bubbled through a young culture of yeast in Laurent's medium for a few minutes and then examined in the manner mentioned above. Concurrent with this flocculation there was an inhibition of growth in the yeast culture as was to be expected. Ethylene oxide then, is a direct narcotic. As a matter of fact, chloroform and ether are always administered in the gaseous state so properly speaking they also belong to this class.

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[1] Ber., **30**, 2668 (1898).

[2] Am. J. Physiol., **1**, 210 (1898).

[3] Am. J. Physiol., **1**, 210 (1898).

[4] Biol. Reviews, **4**, Nr. 4 (1929).

[5] Private conversation with W. D. Bancroft.

[6] Ind. Eng. Chem., **20**, 805 (1928).

The action of nitrous oxide on living organisms is very interesting. If the partial pressure is kept very near one atmosphere the gas will narcotize the higher forms of life in a short time. The singular thing about nitrous oxide is that it has no effect on the lower forms of life unless the pressure is raised very high, i.e., about 45 atmospheres. Furthermore, it has little or no effect on the anaerobic forms of life.[1]

This is indeed exceptional, for in the series of direct narcotics of low molecular weight the specificity is very low. That is, ether and chloroform, etc., act on both the higher and lower forms of life and in addition will also affect plant protoplasm; whereas, nitrous oxide will only act on the higher forms of animal life. The fact that it shows so little effect on anaerobic organisms seems to indicate that its effect is linked up with the oxygen assimulation. This suspicion is strengthened by the fact that, in general, nitrous oxide affects only animals that carry on respiration through haemoglobin.

Thus one would be led to believe that nitrous oxide is an indirect narcotic. That is, it will not flocculate colloids within itself. This is in keeping with its physical properties. A. Findlay[2] found that there was no marked change in solubility of nitrous oxide in solutions of various colloids, i.e., no great adsorption. In this laboratory yeast cultures were exposed to the gas for several days and then examined under the ultramicroscope, there was not the slighest indication of flocculation. Naturally, the gas did not inhibit the growth of the cultures, since the cell colloids were not altered.

If nitrous oxide interferes with the oxygen metabolism it is reasonable to assume that acidic products, that normally would be oxidized to carbon dioxide and water, would accumulate and that these products are responsible for the flocculation. Also, since these products are the normal intermediates it is easy to see why the organism recovers so rapidly when the gas is removed.

In this connection the findings of T. D. Casto[3] that when animals are exposed to nitrous oxide there was a progressive decrease in the haemoglobin of the blood are very interesting. Also, G. W. Crile[4] showed that nitrous oxide caused an increase in the hydrogen ion concentration of the blood, spinal fluid, and bile. This is to be expected.

H. Wieland[5] whose critical study on nitrous oxide led to the discovery of the use of acetylene as an anesthetic, was the first to emphasize the necessity of separating nitrous oxide and acetylene from the narcotics of the alcohol-chloroform type. He points out that these gases have an effect similar to

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[1] H. Wieland: Arch. exp. Path. Pharmakol., **92**, 96 (1922).

[2] J. Chem. Soc., **105**, 292 (1914).

[3] Dental Cosmos, **57**, 881 (1915).

[4] J. Am. Med. Assoc., **67**, 1830 (1916).

[5] Arch. exp. Path. Pharmakol., **92**, 96 (1922).

"mountain sickness." According to his researches he is led to the view that there is an inhibition of oxidation especially in the brain.

Casto's researches[1] are very interesting in explaining the cause of the decrease in oxidation. However, an outstanding physical property of this group of gases, nitrous oxide and acetylene, is their relative greater solubility than other inert gases as Wieland has already pointed out. It may well be that this property would decrease the solubility of the oxygen in the blood serum to such an extent that the haemoglobin can no longer transport the required amount to the cells, although the haemoglobin is not chemically altered.

The theory of Verworn is, this author believes, intimately related to this class of narcotics. The interference with the oxygen transportation will in general lead to narcosis; the cause of this is not the interference, but the flocculation of the bio-colloids by the accumulated waste products. One can readily see that this is just one general method of causing the flocculation. The other is the direct flocculation of the bio-colloids by the narcotic itself. In either case the actual cause of narcosis is the colloidal change that occurs in the cell protoplasm, namely,—a reversible coagulation.

In nature many forms of animals are equipped with such structures and chemicals that they can bring about a narcosis in their prey or enemies. One can readily appreciate the value of such an arrangement as this. Consequently, it is not surprising that man, who was not so favored by nature, at an early period made quite an effort to provide himself with such desirable advantages. We are just now beginning to appreciate the scientific importance of the solution of this problem by our prehistoric ancestors. They found that anesthetics grew on every tree, even the rocks on the ground could bring about this change. In short by simply pounding on their prey with a stick or rock, or better still by a hammer made from both of these, they could cause it to undergo narcosis or even death.

From the point of view of the prehistoric men this was a very great discovery. Since the "narcotics" abounded on every hand and there were no shipping problems or fire hazards and the process of administration so simple that a child could handle the situation it is no wonder that the method met with such widespread favor. In fact it is such a good method that it is still in use today, policemen and thugs often put their patients to sleep by means of the black-jack. Other examples of this phenomenon are the knock-out in boxing or striking our "funny bone" which paralyzes our arm for a few moments.

This is a particularly important phase in the development of the theory of narcosis for it shows two things definitely: that there is no relation between chemical structure and physiological action, and secondly it shows the weakness of other theories of narcosis. Indeed it would be a difficult proposition to show the relation between the chemical composition of black-jacks filled with lead or cotton and the degree of narcosis produced. One can readily see that the chemical composition is secondary, it is only the physical properties that are important. Also there is no relation between boxing gloves and distribution coefficients or surface tensions, nevertheless, boxing gloves can under certain conditions produce narcosis. The theories of Traube, Winterstein, Meyer and Overton, Höber, and Verworn would not predict this.

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[1] Dental Cosmos, 57, 881 (1915).

However, in all fairness to the problem of narcosis, will the theory developed in this paper account for this phenomenon? The theory of coagulation would demand that reversible coagulation take place. There are examples of mechanical agitation causing coagulation; the stirring of fresh blood will coagulate the fibrin. But would mechanical action cause a reversible coagulation of the protoplasm? Heilbrunn[1] answers the question: "In 1910, Lepeschkin described what he called a mechanical coagulation of the protoplasm of Spirogyra. Filaments of Spirogyra were placed under a cover slip and distorted several times by pressure from above. Following this treatment, according to Lepeschkin, the outer protoplasmic layer coagulated and the inner protoplasm broke up into a number of balls. Sometimes the cells burst and the balls passed out into the surrounding medium. After half an hour, all the balls were coagulated too. Lepeschkin's criterion of coagulation is wholly a morphological one, and depends in the main on the appearance of new granules.

"Many authors describe the appearance of vacuoles following mechanical injury. Thus Heilbronn[2] states that mechanical injury produces vacuolization in slime mold plasmodia. Buenning[3] states that countless vacuoles appear in onion cells following mechanical coagulation.

"There are two different ways in which mechanical forces act on protoplasm. Cells may be subjected to pressure insufficient to cause any rupture of the cell membrane, or they may be compressed so as to force out the interior protoplasm until it comes in contact with the outer medium. Cutting and tearing of cells also exposes the interior protoplasm to the surrounding medium. When a cell is cut, torn or compressed so that its protoplasm comes in contact with the outer medium, the naked protoplasm often reacts by forming a film about itself.

"The physical changes occur in protoplasm following an injury to cells in the neighborhood have also been studied by botanists. Heilbronn[4] found that when sections were cut through bean seedlings (*Phaseolus* and *Vicia)*, the viscosity was abnormally high for 10-15 minutes after the sections were made. During this time, the starch grains in the starch sheath cells did not move at all under the influence of gravity, although they moved rapidly enough later. Similar observations have been made by various other workers who have used the gravity method of measuring protoplasm viscosity.

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[1] "Colloid Chemistry of Protoplasm."

[2] Jahrb. wiss. Botanik, **61**, 284 (1922).

[3] Botanisches Archiv, **15**, 4 (1926).

[4] Ber. botan. Ges., **30**, 142 (1912).

"The coagulation or increase in viscosity is reversible. Thus in *Tradescantia*, centrifuge tests showed that 6-7 minutes after cutting the viscosity had returned to normal. When, however, thin sections were made, a longer time was necessary for recovery. Under these conditions, in *Tradescantia*, the viscosity only returns to normal within ten minutes at the earliest. In a similar experiment with *Raphanus*, the return to normal required thirty minutes. Buenning points out that a longer time is necessary for recovery than for the development of maximum viscosity.

"The increase in viscosity following a cut through the stalk is quite considerable. In the cells of *Secale*, one minute after the cut, the viscosity rose to four times its original value. In *Tradescantia*, after half a minute, it rose to three and a half times the original value; and in *Raphanus*, after two and a half minutes, the viscosity was at least five or six times as great, as before cutting."

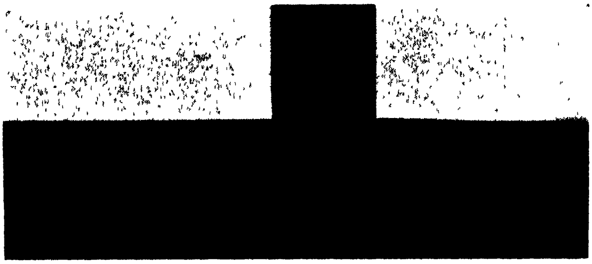

FIG. 10
Mechanical coagulation (Marinesco).

Fig. 10 is a reproduction of Marinesco's photograph showing mechanical coagulation in the nerve cell.

Practically all the theories of narcosis in the ultimate analysis are theories of coagulation. The "membrane theories" postulate that the cell membrane will become permeable or impermeable, to fit the data, and the process by which this is accomplished is usually coagulation. Other theories postulate a lipoid structure to such necessary membranes and then show that the effect will be a function of the distribution between the body fluids and the lipoids, still other theories postulate that the drugs will concentrate just at the proper membrane by surface tension forces. They differ among themselves in the manner in which the narcotic is conveyed to the critical membrane. The photographs in this discussion, showing the effects of narcotics upon nerve cells, were produced by G. Marinesco, a man of unquestionable ability and technique, and *they do not give the slightest indication of coagulation at any boundary in the cell that could possibly be considered as a membrane.* Also the work of Heilbrunn and others shows directly that the coagulative effects are in the *interior* of the cells.

It is pointed out that the other theories of narcosis do not give a complete picture of the cell during narcosis. Therefore, as theories of narcosis they are inadequate.

In the first part of this paper it was pointed out that numerous workers had observed characteristic changes in the viscosity of the cell during narcosis. It is desirable that a working hypothesis of this phenomenon be suggested and to determine whether any conclusions can be drawn from it. The narcotic decreases the viscosity of the cell during the narcosis, higher concentrations of the drug will cause the viscosity to pass through a minimum and return above normal.

Einstein[1] has deduced an equation for the viscosity of sols which holds only under certain conditions: the particles should be spherical, elastic, and large in comparison with the molecules of the dispersing medium. The equation relates the viscosity of the disperse system to that of the dispersion medium and the volume of the dispersed particles. In applying this equation to many biocolloids there is a wide deviation from the actual values, the calculated values being too small. Kruyt[2] suggests that this discrepancy can be best explained through the assumption that the particles are hydrated and have a larger volume than that calculated for the dry particles.

It is well known that most bio-colloids are highly hydrated and consequently they are classed as lyophile colloids. Such colloids have a layer of water around the micellae that is commonly called the water sheath. The water that makes up this sheath is not free but is bound to the surface of the particles. In the first phase of coagulation the narcotic is adsorbed upon the colloidal substrates of the cell and displaces the material that was previously adsorbed there. This amounts to an increase in the effective concentration of these substances. Hence as the narcotic is adsorbed the water sheath and other substances will be progressively displaced. This increase is the amount of the free water will have the same effect on the viscosity of the sol as dilution, i.e., a decrease. The decreasing volume of the particles, due to the loss of the water sheath, will also decrease the viscosity. So it is not difficult to understand why, with increasing small amounts of the narcotic there will be a continuous decrease in the viscosity.

Another factor that might contribute to the decreasing of the viscosity would be the dissolving of fat globules or of films of fat by the anesthetic. However, this is not very general, for simple physical effects such as heat and cold will cause the same type of change.

Smoluchowski[3] has pointed out another correction to the viscosity equation, that of the charge on the particles. In case the particles are charged, they are surrounded by a repelling sphere whereby their active volume is virtually increased. In the initial phase of the coagulation the discharging of the particles will also contribute to the lowering of the viscosity. However, this electro-viscous effect will not be very large unless the particles are small and the specific conductivity of the medium is low.

As soon as the charge on the particles is lowered to such a value that flocculation occurs the particles come together to form the agglomerates.

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[1] Ann. Physik, **19**, 289 (1906); **34**, 591 (1911).

[2] "Colloids" (1927).

[3] Kolloid-Z., **18**, 190 (1916).

Considerable water is trapped in the voids and interstices of these structures, and this water can no longer be counted as free water. Hence as the coagulation progresses the amount of free water is lowered which causes the increase in viscosity. Also the chain structure of the material, as in jellies, would tend to increase the viscosity. So both phases of viscosity are changing aspects of the phenomena of coagulation.

The viscosity variations of the protoplasm of marine eggs, when exposed to various narcotizing agents, have been extensively investigated. In this connection the following quotations from Heilbrunn are of interest.

"Heilbrunn studied the effect of ether and other fat solvents on the protoplasm of sea-urchin eggs. Using the centrifuge method, he was able to show that various fat solvents caused a decrease in viscosity when present in certain dilute concentrations. In somewhat higher concentrations, they produced a coagulation with a great increase in viscosity. The decrease in viscosity produced by dilute solutions of fat solvents was always reversible. On the other hand the coagulation caused by the more concentrated solutions was always irreversible and involved the death of the cell. In a later chapter it will be shown that the decrease in viscosity produced by the fat solvents is related to the anesthetic action these reagents have in preventing cell division in the sea-urchin egg. For the present we are concerned only with the physical action of the fat solvents, and not with any physiological correlations.

"The action of fat solvents has been carefully studied in the starch sheath cells of bean plants, in sea-urchin eggs, in slime mold plasmodia, in the leaf cells of Elodea, and in the stalk cells of Callisia repens. The results on all these different types of protoplasm are fully concordant, and it can now be regarded as scientific fact that, in general, dilute solutions of fat solvents cause a decrease in protoplasmic viscosity, whereas more concentrated solutions cause increase in viscosity or coagulation.

"In 25% distilled water, the viscosity of the Arbacia protoplasm is about 60% of its normal value. In 2½% ether, it will be remembered, the viscosity drops to 53% of what it is in the controls. Moreover, just as in higher concentrations of ether coagulation occurs, so too as the concentration of the distilled water increases beyond a certain limit, there is a sudden coagulation of the protoplasm. It is certain, therefore, that when the protoplasm of the sea-urchin egg becomes diluted with distilled water, there is actually a pronounced decrease in viscosity. This is quite comparable to the effect of ether.

"Concerning the coagulative action of more concentrated solutions of fat solvents, we now have some real information. This coagulative action can be seen morphologically to be accompanied by certain distinctive visible changes. In Arbacia eggs, for example, there is a very noticeable loss of pigment from the pigment granules of the cell, and this is soon followed by the appearance of numerous vacuoles throughout the protoplasm. All these changes are associated with a very definite and characteristic series of reactions which are found not only in sea-urchin eggs, but in other cells as well.

The fat solvent, when present in sufficient concentration, can initiate this series of reactions, and the ultimate result is a coagulation of the protoplasm."

In order to better correlate the viscosity changes with reference to coagulation the following experiments on inorganic sols are of interest. It is now known that the rays from radio-active substances can coagulate many sols.[1] The β rays are quite effective in coagulating positive sols such as hydrated ferric oxide, ceric oxide sols, and alumina sol. Fernau and Pauli[2] have carefully investigated the effects of radium salts on ceric oxide sols. The radioactive material was placed in a tube; the tube was then dipped into the sol. Twenty percent of the β radiation was able to penetrate about 2.5 cm of the sol. In 24 hours exposure the material coagulated to a stiff jelly. The unexposed sol, when left to itself, showed no tendency to coagulate for over a year.

The reason this study is so important is due to the fact that the viscosity variations, due to the coagulation, can be observed without introducing any other substances which in themselves would influence the viscosity.

The variations in viscosity of the above sol during the coagulation period are quite interesting. The same type of changes are observed as in coagulating protoplasm; at first there is a distinct decrease in viscosity. This was followed by a strong rise in viscosity. The decrease in viscosity is explained by the discharging of the particles, as is to be expected in accordance with the theory of Smoluchowski discussed above. The increase in viscosity occurs upon the association of the flocculi. This same type of coagulation can be produced by adding an electrolyte such as sodium chloride.

The most interesting thing about the viscosity changes and coagulation is that the radium radiation causes only the *decrease* in viscosity. If the tube of radium is withdrawn at the moment when the viscosity is at a minimum, the rise in viscosity occurs just the same. This is conclusive proof that the decrease in viscosity is the preliminary stage of coagulation and is just as characteristic of the coagulation as the increase in viscosity. The variations of viscosity merely show the *successive* phases of coagulation.

These cases of coagulation are quite clear, and there can be little doubt but that the process is a simple discharge and coagulation of the sol.

Since this action of radium is so clear-cut, let us investigate its effects on protoplasm. Heilbrunn has already summarized the literature: "Similar effects have been found to follow radium treatment. Thus Forbes and Thacher found a decrease in viscosity of the protoplasm of the eggs of Nereis (an annelid), following treatment with radium. In their own words, "Nereis eggs radiated with β rays, fertilized, and then centrifuged from 7 to 65 minutes after fertilization, show slightly sharper separation of resulting zones than is found in unradiated controls." The difference is most easily explained as due to decreased viscosity of the protoplasm in consequence of radiation.

"Williams studied the effect of beta and gamma rays of radium on the protoplasm of Saxifraga umbrosa. Short exposure caused an increase in the amplitude of the Brownian movement of the small particles of the protoplasm, together with an increase in the rate of protoplasmic streaming. Evidently a decrease in viscosity is produced. Longer exposure to radium caused visible coagulation, and vacuolization of the protoplasm. Comparable results were also obtained by Zuelzer and Philipp on ameba. These authors found that short exposures to radium caused an increase in the speed of ameboid movement, longer exposures resulted in a coagulation of the protoplasm."

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[1] Compt. rend., **138**, 521 (1904).

[2] Kolloid-Z., **20**, 20 (1917).

In the face of such evidence as this, we can feel certain that the variations in viscosity are trustworthy indicators of the series of changes that occur in coagulation. As is to be expected, the preliminary phase of coagulation, i.e. the stage of decreased viscosity, is easily reversible, while the later stage of increased viscosity is more difficult to reverse. Since the colloid theory is concerned with the reversible type of coagulation it is not surprising that narcosis occurs, as a general rule, in the phase of decreased viscosity.

It should be noted that in the first phase water is liberated, and in the second it may be bound again, though not in the same way. This interchange may not exactly balance, and there is considerable evidence that in certain cases it does not. Kochmann[1] has shown that in many tissues which are under the influence of narcotics, there is an actual loss of water. Knaffl-Lenz[2] showed that in 1/1.5N ethyl alcohol, 1/7.5N diethyl ether 1/50N urethane, 1/100N salicylamide and 1/100N benzamide the volume of red blood cells would decrease without causing haemolysis. Kochmann extended this work to other tissues. A typical experiment is as follows: the gastrocnemius muscle of R. temporaria was placed in an isotonic salt solution, this was used as the control. A similar arrangement was made with another muscle except that various narcotics were added to the salt solution. From time to time the muscles were stimulated by electrical means until it was certain that narcosis had occurred in the muscle which was treated with the drug. The weight of the muscle before and after narcosis when compared to that of the control showed that the narcotized muscle underwent a loss in weight. This change ran parallel to the phenomena of narcosis for if the muscle was placed in a narcotic free solution again it recovered and increased in weight. Table VIII contains some of Kochmann's results.

TABLE VIII

Narcotic	Conc. in Millimols	Loss in weight
Chloroform	4.1	1.9%
Chloral hydrate	6.1	10.7%
Amyl alcohol	20.0	4.3%
Butyl alcohol	66.6	5.4%
Diethyl ether	190.0	2.6%
Ethyl urethane	250.0	3.0%
Propyl alcohol	250.0	3.5%

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[1] "Handbuch exp. Pharmak.," **1**, 499.

[2] Arch. ges. Physiol. (Pflüger's), **171**, 51 (1918); Arch. exp. Path. Pharmakol., **84**, 66 (1918).

However, it must be added that Kochmann preferred to regard this effect as the cause of narcosis.

The antagonism shown by various groups of drugs towards one another is well known. Perhaps, with this brief survey of the state of the colloids under the influence of drugs, we may approach the question from a different point of view. The older theories on this subject are closely related to the theories of narcosis, for it was frequently found that small amounts of two narcotics given were much more effective than one would predict from the algebraical sum of the concentrations. On the other hand cases were found where the effect of the two drugs was less than either alone. The explanation that was frequently advanced was that one of the substances increased or decreased the distribution coefficient of the other, hence the combined effect was greater or less, or that the permeability of the various cell membranes were altered in the necessary way to allow more or less narcotic to enter as the case demanded.

It can be readily seen that these theories are just as sterile as the corresponding theories of narcosis. Another theory is based upon the supposed chemical reaction between the antagonists, thus neutralizing the effect. This belief has been disproved by the fact that if chemical neutralization is taking place there will be some definite molar ratio at which the effect will be abolished and if increasing concentrations, of this definite ratio of drugs, the tissue will be normal; such is not the case however, as Dixon points out that in the atropine-pilocarpine antagonism "a solution of pilocarpine and atropine cannot be prepared in which the effects of both drugs are lost, and what is more surprising is that a mixture can be made which in small doses has a pilocarpine effect and in larger doses an atropine effect."

There is a very close relation between the synergism and the antagonism of drugs, and one reason why this field has been so unfruitful is that the early workers did not fully understand this relationship. It has already been shown that there is no relation between chemical constitution and physiological action and that the effect of drugs, in the general case, is not a chemical but a physical process. Furthermore, since the substances that are exerting this effect act upon the colloids of the cell and must be transported from the body fluids to these substrates, the number of the different substrates and the extent of adsorption upon each are important factors. Furthermore, in considering the effect of mixtures of two drugs it is important to know what is the effect on the adsorption of either of the substances by the presence of the other.

We have already discussed the mechanism by which narcotics can behave as stimulants. Now it is often observed that after a narcotic has produced its effect, another substance, that can behave as a stimulant, if given, will stimulate narcotized area again until it recovers, i.e., the substance behaves as an antagonist. Many theories have been advanced to explain this; but it is clear that this stimulation is exactly like the stimulation produced by narcotics and is clearly a case of displacement. It is evident that there can be no displacement if both drugs are not adsorbed upon the substrate which is effected.

Cases are known where this condition is not fulfilled and other adequate explanations have already been offered by others. Antagonism is concerned with elimination; may be accomplished by increasing the flow of blood, dilation of the capillaries in the affected area, increased ventilation of the lungs if the compounds are volatile, or by purgatives if the substances are eliminated by the intestines, etc. We are not dealing with such cases here, it is only when the elimination from a substrate is brought about by displacement adsorption that it is considered in this presentation.

Consider the simplest possible theoretical case, in which the drug is affecting only one substrate. The possible methods of elimination of the drug have already been discussed in the paragraph on recovery, suppose that these methods of elimination are slow and we desire to hasten it. Another substance is given which will be adsorbed upon the same substrate and displace some or all of the original material, thus increasing its effective concentration so that it may undergo the reactions of detoxication faster or diffuse out more rapidly. This method is very effective provided that the antagonist does not complicate the situation by its own action. It can be seen that the drug has been displaced by another whose physiological action is less but whose adsorption is greater. The extent of adsorption is determined by the concentration, so there will be antagonizing concentrations below which this effect will be very small. If the concentration of the antagonist is increased very much above this value the antagonist will begin to exert its own physiological action. In such displacements there is a mutual hinderance in the adsorption of both substances so for a given concentration both substances will be less active. When the two substances have identical physiological actions in the same concentration then antagonism will not be evident. Also if the elimination of the drug is not hastened by the displacement the effect of the antagonist will only be transient.

Claude Bernard studied a case that illustrates the last point. He narcotized rabbits with ether, then injected hydrocyanic acid and found that the hydrocyanic acid was inactive so long as the ether was present, but upon recovery from the ether the animal became poisoned from the effects of the hydrocyanic acid. Here the ether is more strongly adsorbed than the hydrocyanic acid, so the latter can not exert its toxic effect due to its extensive displacement. On the other hand, the hydrocyanic acid was not rapidly eliminated, so on recovery from the ether its effect was produced, i.e. a case of temporary antagonism. Claude Bernard[1] describes the experiment as follows: "I have in connection with M. Paul Thénard made experiments consisting in injecting into etherized rabbits quantities of anhydrous hydrocyanic acid much greater than the doses which would kill the animals rapidly in the normal state. The rabbits showed no toxic effect so long as they remained unconscious. Poisoning took place when the animals waked up and the anesthetic no longer modified the normal properties of the nervous system." It could hardly be expected that Bernard would know of displacement adsorption at that early date.

However, within the body there are a great number of substrates; if a drug is administered and is preferentially adsorbed, for example, by the motor nerves then narcotizing concentrations will paralyze the motor nerves. If the drug is adsorbed by other nerves or glands, then with increasing concentration all the phenomena of narcosis will be exibited in that tissue. It frequently happens that while most drugs show a preferential adsorption for one tissue they are also adsorbed to a less extent on other tissues. The physiological effect does not become pronounced until relatively high concentrations are reached and it is the symptoms exhibited by the action on these secondary substrates that usually inform us that toxic concentrations have been attained. As an example of this, narcotics will generally narcotize the sensory impulses before the wink reflex of the eye is effected, in higher concentrations the wink reflex is abolished; this fact is often used to ascertain the depth of narcosis.

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[1] "Leçons sur les Anesthésiques," p. 99 (1875).

This is the more general case. Normally, if the drug is in low concentrations its relative adsorption will be greater and the amount adsorbed upon the secondary substrates will be too small to exert a physiological action, so its effect is relatively specific. However, if a drug is given that is strongly adsorbed upon the principal substrate, and relative to the first substance has a lower degree of adsorption on the secondary substrates, the original material is displaced, thus raising its effective concentration. This will cause the displaced material to be adsorbed upon the secondary substrates just as if the actual concentration were as great as the effective concentration produced by the displacement. The drug can now exert its physiological action on these secondary substrates and the total effect on the organism appears to be produced by a high concentration of the first drug minus the effect it normally produces on the principal substrate plus the effect of the displacing drug on the principal substrate, if it is in physiological concentrations.

Morphine is adsorbed and exerts its physiological effect on the cerebral nervous system; in higher concentrations it will affect the sensory nervous system, i.e. this is the secondary substrate. Chloroform is adsorbed by both the cerebral and sensory centers and exerts its effect on both substrates, it differs from morphine in that the difference between the action on the cerebral and sensory systems is less marked. The state of affairs is this: morphine is strongly adsorbed in the cerebral region and to a less extent in the sensory region, chloroform is adsorbed in the cerebral system and to a greater extent than morphine in the sensory area.

Now suppose that an animal is under the influence of a small amount of chloroform; the sensory region will not now be affected and the first manifestations of the action will occur in the cerebral center. If a given amount of morphine is administered to the animal, it will be adsorbed within the cerebral center and exert its physiological effect, it will also displace some of the chloroform and increase the effective concentration of the latter. Now since this cannot exert its own effect in the cerebral region it will be adsorbed and act upon the secondary substrates i.e., the sensory centers. The animal will then be in the same state as if a large dose of chloroform had been given, both the cerebral and sensory centers will be narcotized, provided the original concentrations were great enough. It can be readily seen how small amounts of two similar drugs can have a combined effect greater than either alone.

The above experiment was one that was performed by Claude Bernard,[1] he describes it as follows: "Five years ago, in 1864, I made some experiments on the properties of opium. A dog had been given a dose of chloroform and was just coming out of it, the cornea having already recovered its sensitivity, when we injected under the skin five centigrams of morphine hydrochloride. The animal was soon narcotized, as was to be expected, since we had given him the dose of morphine sufficient to produce this effect; but the extraordinary thing is that the insensibility due to chloroform came back at the same time. It was not surprising that the two effects co-existed because both substances had been administered; but it was very singular that the insensibility due to chloroform should reappear after it had disappeared, since no new dose of chloroform had been given which would account for the return of the anesthesia.

"Here is a dog which was given morphine some time ago. It is in the usual state that morphine produces at first. Its sensitivity or rather excitability is very exaggerated. We make it inhale chloroform in a much weaker dose than would be necessary to anaesthetize it in the normal state and the excitability disappears very rapidly even though it was well above normal at first.

"If a pigeon is given a considerable dose of morphine, there is almost no effect. A slight dose of chloroform will then anesthetize the bird; but, curiously enough, the symptoms are due much more to morphine than to chloroform."

The antagonistic action of many drugs is not different from the simple ionic antagonism observed in colloid chemistry. A large number of drugs are electrolytes and the fundamental work of H. B. Weiser[2] will explain the colloidal aspect of this action. A careful study of (1) the effect of each precipitating ion on the adsorption of the other, (2) the stabilizing action of ions having the same charge as the sol, (3) relative greater adsorbability of ions at low concentrations has led Weiser to conclude that the effect of the first two of these factors will be to raise the precipitating concentrations of mixtures above the additive value while the effect of the third will be to lower the precipitating concentrations below the additive value. It was found that when there is a marked difference in the adsorbability the two substances may show antagonism, that is, there will be a mutual hindrance to both. When the precipitating concentration is practically the same then the combined effect is additive. In displacements that occur in the body the drug can act upon secondary substrates, if it is not rapidly removed, so in this respect it differs from the antagonism shown in the test tube.

If the colloids of a cell are reversibly coagulated and the agent that caused the flocculation is displaced by a substance of weaker flocculation capacity for the given concentration, naturally the bio-colloids are peptized again by the electrolytes. Concurrent with this peptization there will be the return of irritability and consciousness. Now the agents that are responsible for the peptization are the electrolytes within the cells. However, it might be possible that organic electrolytes could bring about this peptization under suitable conditions. In this connection it is interesting that many primary and secondary amines of the aliphatic series will behave as antagonists to acid amides and chloral hydrate.[1] The same phenomenon was observed in connection with cocaine, caffeine, ephedrine, and β-tetrahydronaphthyl amine where it was found that they behave antagonistically to chloral hydrate.[2]

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[1] "Leçons sur les Anesthésiques."

[2] J. Phys. Chem., 30, 20, 1527 (1926).

It is easy enough to understand the how and why of most phases of flocculation and peptization; but it must not be overlooked that other effects always accompany these phenomena in living tissue. When there is a flocculation of the colloids there is also a loss of irritability. What happens when there is a peptization of the cell colloids? This is indeed an important question for the understanding of the action of drugs. Without delving into details it is pointed out that the phenomena of irritability are associated with equilibria phenomena, i.e., as long as the material is in a state of flux tending away from equilibrium it shows various degrees of response towards external stimuli, the nearer the approach to coagulation the more pronounced this effect is. In the equilibrium of the cell that concerns the flocculation-peptization system we know that flocculation is accompanied by a loss of response to external stimuli. Furthermore, the gradual approach to this point is associated with increased irritability; on the same basis then a peptization might be expected to lead to a decrease in irritability.

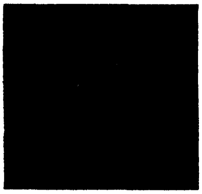

FIG. 11
Sodium iodide
(Marinesco).

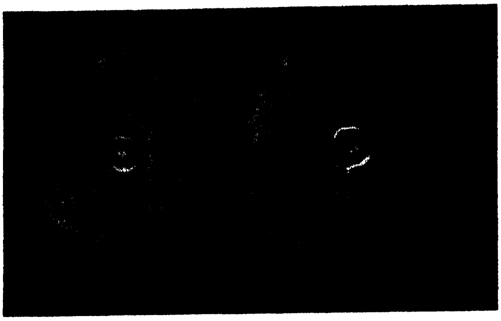

FIG. 12
Antipyrine (Marinesco).

This is no groundless speculation; at the present time there are two things that would indicate whether there was any probability of such a phenomenon. It has been established that sodium bromide has a quieting effect on the nerves, which means that the irritability is lowered. It is also known to colloid chemistry that the bromine and iodine ions can peptize many biocolloids. Fortunately, Marinesco has examined this effect. He found that the colloids of the nerve when exposed to sodium iodide were actually in a state of higher dispersion than normal. Also, antipyrine, which behaves as an analgesic, does identically the same thing. Figs. 11 and 12 are reproductions of Marinesco's photographs showing this peptization. It is impossible at the present time to determine whether this is a general phenomenon but it is very interesting and is an excellent starting point for future research.

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[1] Arch. exp. Path. Pharmakol., **36**, 451 (1895).

[2] Arch. internat. Pharmacodynamie, **23**, 453 (1913); Arch. exp. Path. Pharmakol., **78**, 218 (1915).

Warburg's adsorption theory of narcosis has recently aroused the interest and some favorable criticism from several biological workers.[1] The authors of this paper wish to point out however that this adsorption theory is only a special case of the coagulation theory and, as it is stated by Warburg, is both indefinite and incomplete. Obviously the adsorption of a narcotic by the sols of the affected tissue will tend to do either one of two things: peptize or coagulate the colloids. Warburg forgets to tell us which takes place. The theory of Binz and Claude Bernard is quite definite, it is coagulation. The coagulation theory also recognizes that narcosis can occur without adsorption of narcotics i.e., by heat, cold, electricity, mechanical force, and water. In fact, the last case depends upon a *desorption* of the stabilizing ions. The phenomena of narcosis can be explained only upon the basis of the theory of Binz and Claude Bernard.

In conclusion we can say that the chemistry of anesthesia is the chemistry of sols, gels, displacement adsorption, coagulation, viscosity changes, peptization, adsorption, swelling, and catalysis; briefly, colloid chemistry applied to the muscles, nerves, glands, and cells of the affected tissues. The ultimate effect of a narcotic is the reversible coagulation of the cell colloids. This is preceded by a state of stimulation which depends upon the decreasing stability of the colloids before coagulation.

Summary

(1). The criticisms directed against the theory of Binz and Claude Bernard, that low concentrations of narcotics will not coagulate the cell colloids and further that any coagulation produced is irreversible, have been shown to be wrong; due to the fact that the effect of the electrolytes of the cell were neglected.

(2). It was demonstrated both in vitro and in vivo, by the ultramicroscope, that low concentrations of narcotics flocculate the cell colloids. The coagulation is reversible upon the removal of the narcotic.

(3). The converse of this (2) also follows: a reversible coagulation of the cell colloids, produced by whatever means, will cause narcosis. The cases of narcosis due to heat, cold, electricity, water, and mechanical effects are due to this fact.

(4). The decreasing stability of the colloids at low concentrations of the narcotic is accompanied by an increasing irritability. Thus narcotics in low concentrations should behave as stimulants and stimulants in high concentrations should behave as narcotics. Thus the common aliphatic narcotics are stimulants to growth, motion, chemical reactions, enzyme action, etc. when they are in low concentrations. On the other hand, stimulants such as caffeine and strychnine behave as typical narcotics in high concentrations.

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[1] Physiol. Rev., **10**, 171 (1930).

(5). Narcotizing agents are divided into two groups: direct narcotics, which coagulate the cell colloids by direct action, and indirect agents which interfere with some normal function of the cell such as oxidation, and the coagulation is produced by the accumulated waste products. Ether, chloroform, and alcohol are examples of the direct class and nitrous oxide, acetylene, and hydrocyanic acid behave as indirect narcotics.

(6). The distribution coefficients of the Meyer and Overton theory are to be regarded as a rough measure of the rate of transport of the various narcotics. The relative degree of adsorption determines the extent of coagulation, in other words, the narcosis.

(7). The depression of the surface tension of water by various narcotics (Traube's theory) is to be regarded in the same light as the distribution coefficients.

(8). Verworn's theory is interpreted as a special case of the coagulation theory in that it deals with only the indirect narcotics. The depression of the oxidation alone does not cause the narcosis, the accumulated waste products coagulate the colloids of the cell and are responsible for the effect.

(9). The work of Heilbrunn on the viscosity of protoplasm offers a substantial confirmation to the coagulation theory.

(10). Marinesco's researches on the colloidal structure of nerves also presents a striking confirmation to the salient points of the coagulation theory.

Cornell University

THE CHYLOMICRON EMULSION

BY S. DEW. LUDLUM, A. E. TAFT AND R. L. NUGENT

Introduction

The blood distributes the products of the digestion of protein and carbohydrate in true solution. From the colloidal point of view, it is a matter of great interest that the third important foodstuff, fat, is distributed as an emulsion of minute droplets. Those of measurable size are estimated to be mostly from 0.5 to 1 μ in diameter.[1] Many are smaller than this and are visible only by means of dark-field illumination. These droplets are best known as chylomicrons because they enter the blood with the chyle, a milky fluid containing absorbed food from the intestine which pours directly into the blood stream. Blood containing chylomicrons thus has, in addition to its better known characteristics, that of a lipoid emulsion,[2] which may be called the chylomicron emulsion. Although it is obviously an emulsion system of extraordinary importance, it has received little attention from colloid chemists.

It is the purpose of the present paper to describe such results as have been obtained to date in an investigation of the chylomicrons considered as emulsion particles. It is offered as a contribution to the colloid chemistry of the chylomicrons.

The study of these tiny fat droplets in blood has a truly fascinating history as related by Gage and Fish[3] in their classical paper on the digestion, absorption, and assimilation of fat in the animal body. A brief account of this well precedes the presentation of the particular results of this paper.

Outline of the History of Chylomicron Study

It has been known for about three hundred years that the presence of food in the small intestine brought about the appearance of a milky chyle which poured directly into the blood stream, in turn causing the blood serum to assume a milky appearance. A century and a half later, we find the description of experiments to show that this milky fluid contains an exceptional amount of fat, for, if dried upon a piece of paper, it leaves an obvious grease spot. Hewson,[3] who made this observation, also discovered that the microscopic study of such milky chyle and serum disclosed many exceedingly small particles not present in the clear liquids.

Seventy years preceded the next advance in chylomicron knowledge. Gulliver,[3] in 1840, took up the study of the small particles which had been discovered by Hewson, and described their Brownian motion, and compared them with the fat globules of milk. For some reason best known to himself, he called them "the molecular base of the chyle."

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[1] Gage and Fish: Am. J. Anatomy, 34, 1 (1924); Bloor: Physiol. Rev., 2, 92 (1922).

[2] Ludlum, Taft, and Nugent: Colloid Symposium Annual, 7, 233 (1929).

[3] Gage and Fish: Am. J. Anatomy, 34, 1 (1924).

Modern chylomicron study begins some thirty years after Gulliver with Edwards[4] who in 1877 observed blood with the dark-field microscope and remarked that it appeared as a wholly new substance with multitudes of dancing particles which looked like motes in a sunbeam. Hewson and Gulliver could only have observed comparatively few, exceptionally large chylomicrons in their light-field studies. A proper idea of the number of the chylomicrons and the beauty of their observation was revealed by the work of Edwards. Their similarity in appearance to motes in a sunbeam led to calling them the "haemoconia" or "blood dust."[5] These terms are frequently used to-day.[6] At various stages in their history, the chylomicrons have also been called "elementary granules",[3] "a fine granular dust"[3] and, more correctly, "fat dust."[7]

Even during the past thirty-five years many ingenious and far-fetched explanations have been advanced for the presence of the chylomicrons in the blood, and it was not until the very modern work of Gage and his associates[8] that their true nature became generally known. Gage devised the name "chylomicron" and first applied it to the particles in 1920.[9]

The Question of the Relation of Chylomicron Counts to the Fat Contents of Blood Plasma and Serum

After a meal containing fats, the number of chylomicrons in the blood gradually increases to a maximum and then decreases to the fasting level, practically zero. Fig. 1 is reproduced from the paper of Gage and Fish. The left half represents the dark-field microscopic appearance of a blood drop taken just preceding a meal containing fats and the right half the appearance several hours after fat ingestion. One sees the various elements characteristic of the clotted blood-smear, and notes particularly the rise in number of chylomicrons after the meal. The bright points in the dark field give a very good idea of the appearance of the chylomicrons, but no static picture compares with the actual observation which discloses their rapid and brilliant Brownian motion.

Fig. 2 likewise taken from the paper of Gage and Fish illustrates their method of counting chylomicrons. It shows also a typical curve obtained when chylomicron counts on a series of blood drops are plotted against the lengths of time after a meal containing fats at which the respective drops were taken. It is impossible to count the number of rapidly moving particles in a whole microscopic field, but the number in a small division of a field may be readily observed. Small field divisions are obtained with a net-micrometer ocular. The observation of the number of chylomicrons in a sufficient number of small divisions in a sufficient number of fields with the establishment of an average number, gives a good relative measure of the number of chylomicrons in a given blood specimen.

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[4] Monthly Micr. J., **18**, 78 (1877).

[5] Mueller: Centr. allgem. Path. und Path. Anat., **7**, 529 (1896).

[6] Bayliss: "Principles of General Physiology," Longmans, Green and Company, New York, 375 (1927).

[7] Munk and Rosenstein: Arch. path. Anat. Physiol., **123**, 239 (1891).

[8] Gage: The Cornell Veterinarian, **10**, 154 (1920); Gage and Fish: J. Am. Vet. Med. Assoc., **53**, 384 (1921); The Cornell Veterinarian, April (1921) p. 230; Am. J. Anatomy, **34**, 1 (1924); Gage-Day: Am. J. Surg., **36**, (4) 53 (1922).

[9] The Cornell Veterinarian, **10**, 154 (1920).

The fluid in which the blood cells are contained is called the blood plasma. When blood clots, a jelly-like mass is formed which contains all the cellular elements and a minor portion of the salts and protein from the plasma. This mass contracts and expresses a fluid which is plasma minus the plasma constituents contained in the clot, and is called the blood serum. It has been the subject of a very large number of investigations because it is readily obtained, and because it bears a definite relation to the plasma of the living animal although differing somewhat from the latter in composition.

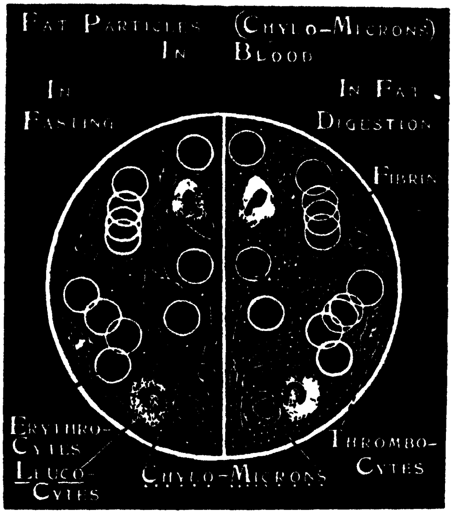

Fig. 1

Fresh blood under the high-power dark-field microscope. The left half after sixteen to twenty-four hours' fast. The right half three to four hours after a meal with plenty of fat. *Chylo-microns* or fat particles. They are numerous in the right half, and few in the left half. *Erythrocytes*, red blood corpuscles. *Fibrin*, the fine, cobweb like filaments present in coagulated blood. *Leucocytes*, or white blood corpuscles. *Thrombocytes*, or blood plates. (Fig. 1 and the accompanying legend are reproduced by permission, from the paper of Gage and Fish: Am. J. Anatomy, **34**, 1 (1924).

If a drop of serum from a blood containing a goodly number of chylomicrons is examined with the dark field microscope, it appears somewhat as shown in Fig. 3. As far as one can observe, the chylomicrons remain in full force in the serum. From the colloid chemical as well as from the biochemical point of view, it is of interest to inquire to what extent chylomicron counts parallel serum and plasma fat determinations. If all the fat in serum or plasma is in the form of chylomicrons of uniform size and, if accurate counts are possible, a chylomicron count could be used as an accurate determination of serum or plasma fat. If, on the other hand, all the serum or plasma fat is in the form of chylomicrons which can be accurately counted and the results of chylomicron counts and fat determinations do not parallel each other, important evidence is furnished as to the variation in size of chylomicrons under different conditions.

Since the paper of Gage and Fish, several people have compared chylomicron counts and the corresponding serum or plasma fat determinations. The general conclusion is that, although a relation between the two is quite apparent, the counting of chylomicrons does not offer a means of determining serum and plasma fat contents with any accuracy. Although further work on this point seems highly desirable, particularly on the basis of results obtained by the authors,[2] the foregoing general conclusion is entirely to be expected simply on the basis of observed variations in the size of the particles. Gage and Fish note that chylomicrons may vary at least three-fold in diameter which represents a twenty-seven fold variation in volume.

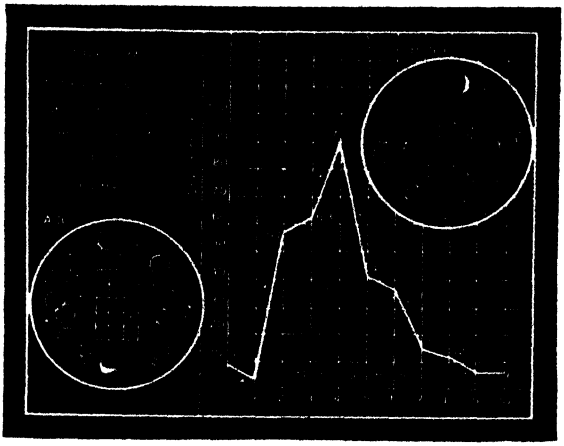

FIG. 2

Chylomicron curve and two microscopic fields to show how the data for the curve were obtained. At the lowest point of the curve there were but three chylomicrons in the net-micrometer, and at the peak of the curve, 91. The numerals along the curve show in the same way how many chylomicrons were in the net-micrometer at the different hours of the experiment. It will be noted that the number at the beginning was 9 and at the end of the first hour three. This means that the previous meal had not been completely assimilated when this experiment began. (Fig. 2 and the accompanying legend are reproduced by permission, from the paper of Gage and Fish: Am. J. Anatomy, 34, 1 (1924)).

Gage and Fish further note a tendency toward increase in particle size at that time after a meal containing fat when the absorption is at its height. This latter observation may well explain the result of Knudson and Grigg[10] that, after a meal containing fat, the maximum chylomicron count precedes the maximum fat content by several hours. If we postulate that the chylomicrons gradually increase in size with the time of absorption to twice their original size, a count of half as many at the absorption maximum as at the chylomicron count maximum might well represent several times as much fat. The conclusion of Knudson and Grigg is confirmed by a comparison of the free-fat contents and chylomicron counts of the plasma of the normal dogs studied by Bloor, Gillette, and James.[11] It affords confirmatory evidence for the observation of Gage and Fish, that the size of the chylomicrons tends to increase with the time of fat absorption.

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[10] Proc. Soc. Exptl. Biol. Med., 20, (8) 462 (1923).

Regardless of its absolute accuracy as a method for serum and plasma fat determinations, there is no question but that the chylomicron count is sufficiently accurate to be a valuable adjunct to such determinations,[11] and affords an extremely useful method for the investigation of the absorption and assimilation of fat both in physiological and clinical studies.[3,12]

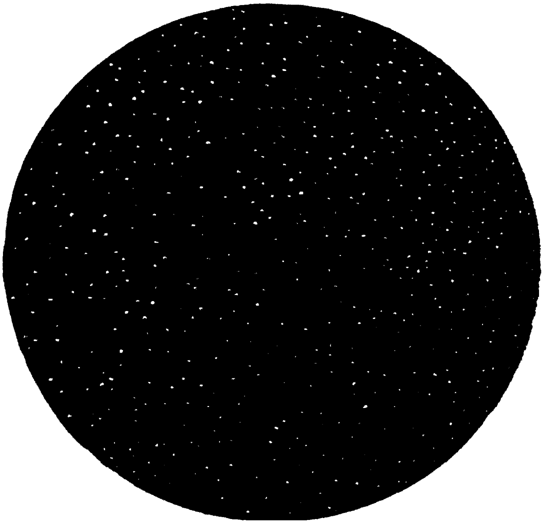

FIG. 3

A drawing to illustrate the dark-field microscopic appearance of blood serum containing chylomicrons. (Oil immersion objective.).

The Question of the Existence and Potential Importance of Surface Films on Chylomicrons

In a recent paper, the authors[13] discussed the dual colloidal aspect presented by human blood serum containing chylomicrons. It is not only a protein solution as ordinarily considered but also a lipoid emulsion and hence of exceptional interest from the two points of view.

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[11] J. Biol. Chem., 75, 61 (1927).

[12] Schilling: "The Blood Picture" (Translation by Gradwohl) The C. V. Mosby Co., St. Louis, 38 (1929); Hubbard: J. Biol. Chem., 55, 357 (1923); Schroeder and Holt. Am. J. Dis. Children, Feb., 1926, p. 201; MacArthur: J. Biol. Chem., 87, 299 (1930).

[13] Ludlum, Taft, and Nugent: Colloid Symposium Annual, 7, 233 (1929); See also Ludlum and Taft: Alexander's "Colloid Chemistry," The Chemical Catalog Co., Inc., New York, 2, 695 (1928).

So far as could be determined at that time, there was no record of any investigation directed toward the determination of the stability factors involved in the chylomicron emulsion and even no discussion of their possible nature and importance.

Oil-in-water emulsions which may be as concentrated as the chylomicron emulsion, always involve a third substance, the emulsifying agent which concentrates in the oil-water interface, forming a film around the dispersed oil droplets and preventing their coalescence.[14] Knowing the composition and size of the chylomicrons and the reason for their existence, the remaining all-important question from the emulsion point of view is that of the nature of their surface films.

On the physiological side these films determine the stability of the chylomicrons in the plasma and thus the very act of transportation by the blood. The physiology of the assimilation of food fat from the blood and its storage and final utilization is by no means an open book.[1] It is highly probable that the discovery of the nature of the surface films on the chylomicrons would be of importance in the future study of these problems. It seems quite likely that the chylomicrons may be taken up as such by cells. In this case their surface properties, that is the properties of the substance which forms their surface films, are all important.

It has been shown[15] that acid-fast bacteria, which have lipoid-like surfaces, are not readily taken up by phagocytic cells. However, when they are treated with the proper serum, a protein film forms around them, and they are then readily phagocytized. In other words, the cell material must wet the bacterium in order to enclose it; it is able to wet a protein surface but not a lipoid surface. By analogy, the whole process of the removal of food fat from the blood may depend upon the presence of protein films around the chylomicrons which may be wet by the material of the assimilating cells.

In storage tissues, fat is often found in droplets much larger than chylomicrons. Apparently the tissue cells bring about the coalescence of chylomicrons. To do this, they must act upon whatever films may be present around them. The final utilization of food fat must apparently also often involve the destruction of protective films around the chylomicrons, since such films must be removed before the chylomicron fat can be saponified or otherwise acted upon chemically. If the films consist of protein, there is a ready mechanism for their destruction in the action of proteolytic enzymes within the cell.

Furthermore as previously mentioned by the authors,[2] a knowledge of surface films on chylomicrons may be useful in the study of the serum diagnosis of syphilis. The precipitation tests appear to involve the addition of a suspension of lipoid droplets to blood serum.[16] If the serum is syphilitic, the drops aggregate and if non-syphilitic, they remain dispersed. The aggregation or non-aggregation of the droplets presumably depends upon differences in the nature of the surface films which form around them in the two cases. The naturally occurring surface films on native lipoid droplets in the serum may well bear some relation to those which form around the droplets of so-called antigen suspension.

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[14] Bancroft: "Applied Colloid Chemistry," McGraw-Hill Book Co. Inc.,, New York, 351 (1926).

[15] Mudd, Lucké, McCutcheon and Strumia: Colloid Symposium Monograph, 6, 131 (1928); J. Exptl. Med., 52, 313 (1930); Strumia, Mudd, S., Mudd, E. B. H., Lucké and McCutcheon: J. Exptl. Med., 52, 299 (1930).

[16] Kahn: Alexander's "Colloid Chemistry," 2, 757 (1928).

Thus it appeared that the study of the surface films on chylomicrons was by all means the next important step in the study of chylomicrons as abstract emulsion particles, and further might well be of value in special physiological and pathological studies. Because of these facts it seemed important to follow up preliminary results reported last year,[2] in order better to establish the existence of protective films around the chylomicrons and to learn more of their nature.

All the experiments have been done with chylomicrons in human blood serum. In view of the results obtained, it is believed that the extension to human plasma and to the serum and plasma of animals should be a relatively simpler matter. Blood was taken in Keidel tubes, allowed to clot, and then centrifuged to separate the clot and the serum. The serum was either removed with a syringe for immediate use or with a second Keidel tube for storage in the ice chest.

The Isoelectric Point of the Chylomicrons determined by a Maximum Flocculation Method

When an emulsion particle is coated with a film of protective agent its surface properties should presumably be those of the film-forming substance. An interesting case demonstrating this to be a fact is that of lecithin sols.[17] The pure sols show a maximum flocculation tendency at pH 2.3. If a little albumin is added to the solution, this value changes to pH 4.7, the isoelectric point of albumin; and, if globulin is added instead of albumin, it changes to pH 5.3, close to the isoelectric point of globulin. The protein in each case forms a film over the lecithin surface of the particles.

This case not only illustrates the point but is peculiarly applicable to the chylomicron problem. An examination of the composition of human serum[18] indicates that the two major constituents well known as protective agents in oil-in-water emulsions[19] are lecithin and protein. It would appear from the foregoing paragraph that, even though lecithin tended to concentrate in the chylomicron-plasma interface, protein would in turn concentrate in the resulting lecithin-plasma interface and the surface properties of the chylomicrons would be those of protein.

The obvious thing to do was to attempt to determine the isoelectric point of the chylomicrons to see whether it occurred in the region pH 4.7 − 5.4, characteristic of the serum proteins or, for example, in the region pH 2.0 – 3.0, characteristic of lecithin. The first attempt was by means of a maximum flocculation method.

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[17] Höber: "Physikalische Chemie der Zelle und der Gewebe," Wilhelm Engelmann, Leipzig, 752 (1926).

[18] Gram: Am. J. Med. Sci., **168**, 511 (1924).

[19] Seifriz: Am. J. Physiol., **66**, 124 (1923).

The pH of serum is about 7.4. As a preliminary experiment equal volumes of different strengths of hydrochloric acid from N/16000 to 4 N were mixed with sera containing chylomicrons on a microscope slide. It is important that not more than an equal volume of acid be added, because greater dilution than this may lead to the precipitation of globulin in the isoelectric region. Each preparation was then covered with a cover glass which was sealed with vaseline or paraffin. After a definite time interval, examination was made for signs of flocculation of the chylomicrons using the dark-field microscope with an oil immersion objective. In this way it was determined that there was indeed a definite maximum flocculation zone corresponding to mixtures of sera with acid strengths of the order of thirtieth normal. As implied, in mixtures with somewhat stronger hydrochloric acids the chylomicrons remained dispersed. This qualitative observation of a maximum flocculation zone was made on a large number of sera.

The next question was as to the pH of the maximum flocculation mixtures. Equal volumes of sera and the acids which gave a maximum flocculation mixture were mixed in small test tubes and the pH of each resulting mixture determined electrometrically. Fifteen such determinations gave values ranging from about pH 4.0 to 6.0 with an average pH of 5.1. The pH of the maximum flocculation of the chylomicrons was thus in the range of those of particles coated with protein films rather than of particles with lecithin surfaces.

Serum protein consists very largely of serum albumin whose isoelectric point is at pH 4.7[20] and serum globulin whose isoelectric point is at pH 5.4.[21] The average isoelectric point as determined above lies between these two values, but the fact could not be considered significant because of the wide variation of the values from this mean. Obviously a more accurate method was needed to definitely establish the isoelectric point to be in the protein range.

If this could be found, the possibility existed that a sufficiently definite value might give information as to the particular protein or proteins forming the protective films. Thus an isoelectric point very close to pH 4.7 would afford strong indication that the chylomicrons were coated with films of serum albumin. Likewise an isoelectric point very close to pH 5.4 would point to serum globulin as the important constituent. Any intermediate value would be open to interpretation as due to films of mixed albumin and globulin and, finally, values higher than pH 5.4 or lower than pH 4.7 would quite definitely indicate the presence of a third constituent.

It was decided to add N/10 hydrochloric acid gradually to about 2 cc. of serum into which dipped a Hildebrand hydrogen electrode and the salt bridge connection from a saturated calomel electrode for the electrometric determination of the pH at each state of the titration. A Leeds and Northrup type K potentiometer was employed and the electrodes were platinized according to the method of Popoff, Kunz, and Snow.[22] To test the technique of electrode preparation and the entire potential measurement system, three electrodes were prepared and used to measure the pH of N/10 hydrochloric acid; 1.037 being taken as the correct value. The three electrodes checked each other to within a fifth of a millivolt and the accepted value for the pH of the solution to within 0.01 pH.

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[20] Michaelis and Davidsohn: Biochem. Z., **33**, 456 (1911); See Mudd: J. Gen. Physiol., **7**, 389 (1924-25) for a valuable table of isoelectric points.

[21] Rona and Michaelis: Biochem Z., **28**, 193 (1910).

After each addition of the acid the system was allowed to come to equilibrium and the pH read. A drop of the mixture was then examined with the dark-field microscope for signs of flocculation of the chylomicrons.

Ordinarily in making determinations of the pH of maximum flocculation, the disperse material is suspended in a series of buffer solutions. After a definite time, the degree of flocculation in each solution is determined by macroscopic observation. A separate portion of the suspension to be examined is required for each pH value. The method described above has the advantage,

TABLE I

The Flocculation of Lecithin Sols on Gradual Acidification with N/10 Hydrochloric Acid

Sol	pH	Flocculation
One per cent lecithin in distilled water.	5.60	—
	5.35	—
	4.80	—
	3.90	—
	2.70	++
	2 30	+++++
One per cent lecithin in Ringer's solution.	8.20	–
	6.90	–
	6.30	–
	5.40	–
	4.75	–
	3.50	+
	2.60	+++++
One per cent lecithin in five per cent egg albumin solution.	8.70	–
	7.06	–
	6.52	–
	6.02	+
	5.50	+
	5.17	+
	4.80	+++
	4.50	+++++

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[22] J. Phys. Chem., 32, 1056 (1928).

when working with a limited supply of material, that one sample is used successively at different pH values. It further rules out any possible effects of foreign buffer salts, and the microscopic feature allows the observation of flocculation conditions which would not be macroscopically visible. It has the disadvantage that there is danger of "lag" in going from one pH value to another, which becomes a certainty in case irreversible transformations occur.

It was decided to try some preliminary experiments with lecithin sols. One per cent sols were prepared, according to the method of Porges and Neubauer,[23] in distilled water, Ringer's solution, and five per cent egg albumin solution. If a flocculation were obtained only at pH 2.0—3.0 in the case of the protein-free sols and close to pH 4.7 in the case of the sol containing albumin, the experiments would not only be an interesting example of the applicability of the titration method, but also confirm the results reported in the literature as to the formation of protein films on lecithin surfaces.[17] Furthermore it was of interest to know what effect the salts of Ringer's solution might have upon the pH of maximum flocculation of lecithin sols, since the value pH 2.3 was reported for a fairly pure sol. The results are shown in the foregoing table.

The results in Table I indicate the usefulness of the method and confirm the shift of the flocculation zone from pH 2.0 — 3.0 to the isoelectric region of albumin when the protein is added to the solution, indicating that a protein film has formed around each lecithin particle. They further show that, so far as the purposes of the present investigation are concerned, the salts of Ringer's solution have a negligible effect upon the pH flocculation of lecithin sols.

Two runs were next made with sera containing chylomicrons with results, as in the case of the lecithin experiments based simply upon a general observation of the relative number of aggregates and of single particles in each preparation. To eliminate the possibility of error due to "lag" in redispersion the first serum was gradually acidified and the second immediately taken to, pH 4.05 with a drop of stronger acid, and then titrated back with tenth normal sodum hydroxide solution. The results are shown in Table II.

TABLE II

The Flocculation of Chylomicrons at Different pH Values

Serum Number 1		Serum Number 2	
pH	Flocculation	pH	Flocculation
7.25	—	7.25	—
6.70	—	4.05	—
5.90	+	4.50	—
5.40	+++	4.60	+
5.22	+++	4.70	+
4.90	+++++	4.85	+++
4.65	++++	5.04	+++++
4.40	+++	5.24	++++
3.62	+	5.66	+++
		6.20	+

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[23] Biochem. Z., 7, 152 (1907-08).

The first run indicates a maximum flocculation between pH 5.22 and 4.65, and the second between pH 5.24 and 4.85, both lying very definitely between the isoelectric points of the two serum proteins.

It was highly desirable to check the results of Table II by some quantitative method. It seemed best to use particle counts as a measure of the degree of flocculation in any preparation. The chylomicrons and their aggregates were the only visible particles. Obviously the greater the aggregation of the chylomicrons in any case, the smaller the relative particle count. The counts were made in a similar manner to the chylomicron counts of Gage and Fish[3] which have been previously described. Two further sera were run on this basis using a slightly different procedure with regard to the time factor in the two cases. In the first, after each regulated addition of acid and attainment of a constant pH value, the serum was allowed to stand for one half hour before the drop was removed for immediate examination. In the second, the drops were removed immediately after attainment of a constant pH value, but were then allowed to stand over night under sealed coverslips before counting. The results are shown in Table III.

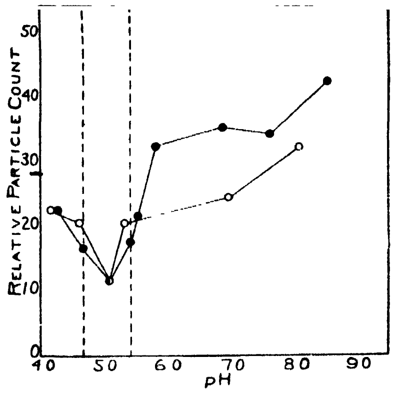

FIG. 4
Particle counts plotted against pH values in the determination of the maximum flocculation of chylomicrons.

TABLE III

Quantitative Data on the Flocculation of Chylomicrons at Different pH Values

Serum Number 3		Serum Number 4	
pH	Relative Particle Count	pH	Relative Particle Count
8.50	43	8.05	33
7.60	35	6.93	25
6.85	36	5.30	21
5.80	33	5.07	12
5.51	22	4.62	21
5.40	18	4.16	23
5.08	12		
4.66	17		
4.28	23		

The results of Table III are plotted in Fig. 4, where the ordinates are relative particle counts and the abcissas are pH values. The points for serum number three are shown as dots and those for serum number four as circles. Both runs clearly indicate a maximum flocculation zone at pH values between those of the isoelectric points of serum albumin and serum globulin, which fact in turn indicates that the isoelectric point of the chylomicrons lies within this range.

The Isoelectric Point of the Chylomicrons determined by a Cataphoretic Method

There is every reason to believe that the pH of maximum flocculation of chylomicrons is also that of their isoelectric point. It seemed necessary however to check this fact by demonstrating that the sign of their surface charge reversed approximately in this pH range. If their isoelectric point in serum lies between those of serum albumin and serum globulin, they should be positively charged at pH 4.7 and negatively charged at pH 5.4. It is apparent that checking this point amounts to a second determination of their isoelectric point. Fortunately a well-known method and standard apparatus are available which may be applied to the determination of the isoelectric point of chylomicrons by a cataphoretic method.

Portions of serum containing chylomicrons were diluted fifty times with a series of fifth molal sodium acetate-acetic acid buffer solutions covering the range from pH 4.4 to 5.6 at 0.2 pH intervals. The direction of migration of the chylomicrons in each buffer mixture was observed in a Northrop-Kunitz[24] microcataphoresis cell with arrangement of accessory apparatus according to Mudd.[25] Observations were made at the levels where electrical endosmotic effects are theoretically negligible.[26] The object in each determination was to find two successive buffer mixtures between which reversal of the sign of charge of the chylomicrons took place.

Preliminary experiments were run using the lecithin emulsions in Ringer's solution and five per cent egg albumin solution in place of serum. The results of these are shown in Table IV.

TABLE IV

The Direction of Migration of Lecithin Emulsion Particles in Buffer Solutions

Buffer pH	Particles from 1 per cent lecithin emulsion in Ringer's solution	Particles from 1 per cent lecithin emulsion in 5 per cent egg albumin solution
5.0	To anode	To anode
4.8	To anode	To anode
4.6	To anode	Practically motionless
4.4	To anode	To cathode

At pH 4.4 the emulsion particles from Ringer's solution were still strongly negatively charged, while those from the five per cent albumin solution had reversed sign at approximately pH 4.6, and were definitely positively charged at pH 4.4. These results are obviously in agreement with the flocculation results obtained with lecithin sols.

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[24] Colloid Symposium Monograph, 6, 134 (Footnote) (1928).

[25] The cell with accessory apparatus may be obtained from the Arthur H. Thomas Company, Philadelphia.

[26] Von Schmoluchowski in Graetz: "Handbuch der Elektrizität und des Magnetismus," 2, 366 (1921).

Four determinations were next made on three sera with the results as shown in Table V.*

TABLE V

The Direction of Cataphoretic Migration of Chylomicrons in Buffer Solutions

Buffer pH	Serum A	Serum A′	Serum B	Serum C
6.0	To anode	To anode	To anode	To anode
5.0	To anode	To anode	To anode	To anode
5.6	To anode	To anode	To anode	To anode
5.4	To anode	To anode	To anode	To anode
5.2	To anode	To anode	To anode	To anode
5.0	To anode	To anode	To cathode	To anode
4.8	To cathode	To cathode	To cathode	To cathode
4 6	To cathode	To cathode	To cathode	To cathode
4.4	To cathode	To cathode	To cathode	To cathode

In three cases the isoelectric point of the chylomicrons was shown to lie between pH 4.8 and 5.0 and in the fourth between pH 5.0 and 5.2. They are all in striking agreement with those obtained by the maximum flocculation method, and establish the conclusion that the isoelectric point of the chylomicrons in human serum lies between the accepted isoelectric points of serum albumin and serum globulin in the seven cases studied.

There is thus no question but that the isoelectric point of the chylomicrons in human serum lies in the range of those of the serum proteins. Isoelectric-point evidence is probably the strongest which can be brought to prove the presence of protein films on chylomicrons. A possibly correct, and at least an interesting interpretation of the position of the isoelectric point between those of the serum proteins, is that the protein films consist of a mixture of serum albumin and serum globulin.

According to Mudd,[27] acetate buffers have little effect in shifting the pH of the isoelectric point of protein surfaces. The agreement of the values obtained for the isoelectric point of the chylomicrons determined by the maximum flocculation method involving no addition of buffer salts and by the cataphoretic method involving the suspension of the chylomicrons in acetate buffer solutions is interesting as in agreement with this point of view.

The Destruction of the Surface Films on Chylomicrons

Since the chylomicrons are emulsified droplets of fat it should be possible to cause them to coalesce to form larger drops. It will be remembered that this is apparently what may happen in tissues which store fat. Analogous experiments with chylomicrons in serum would be interesting from this point of view.

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* Determinations have since been made with chylomicrons from three more sera. The reversal point was between pH 4.8 and pH 5.0 in each of these cases.

[27] J. Gen. Physiol., 9, 73 (1925-26).

Furthermore, if the chylomicrons are surrounded by protein films, we should expect that reagents which precipitate protein or otherwise alter its properties would be effective in causing such coalescence. If they are, we have independent evidence of the existence of protein films.

It is apparently quite generally agreed that the fat drops in milk are surrounded by protein films which recent work indicates may consist of casein.[28] It has been known for a long time that it is quite difficult to extract milk fat with ether until acid, alkali, or rennet has been added, presumably to destroy these films.[28] According to Bancroft,[14] protective films of a substance may not form under conditions which cause the salting out of that substance. Presumably if present they would become dehydrated and brittle, and proceed to crack with coalescence of the emulsion droplets.

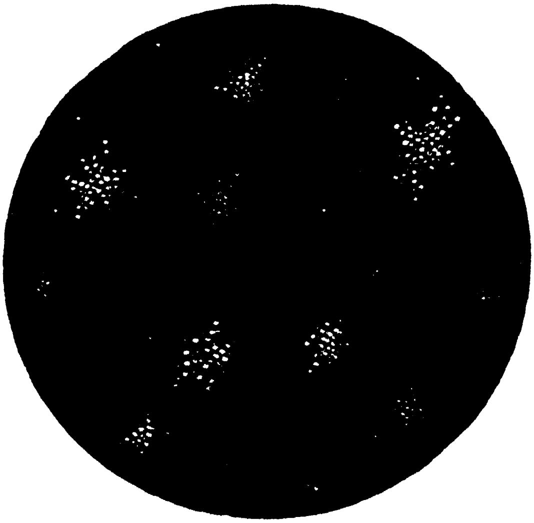

FIG. 5

A drawing to illustrate the mode of aggregation of chylomicrons at their isoelectric point.

The first experiments in connection with the isoelectric flocculation of the chylomicrons lead to evidence on this point. The isoelectric flocculation occurred when equal volumes of serum were added to about N/30 hydrochloric acid. With strengths from N/30 to about N/8 acid, the chylomicrons were dispersed as positively charged particles. In all cases with 2 N acid, copious precipitation of protein occurred presumably due to a "salting-out" action of the concentrated acid.

With strengths between N/8 and 2 N acids, an interesting phenomenon was noted, best observed after the sealed preparations had stood for at least an hour. A combined coalescence and aggregation of the chylomicrons apparently occurred. A good impressionistic idea of the difference in appearance between the isoelectric aggregates and these coalesced aggregates is given by

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[28] Titus, Sommer and Hart: J. Biol. Chem., 76, 237 (1928).

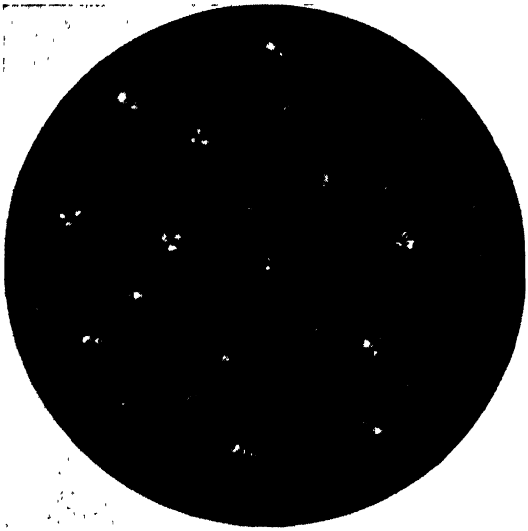

FIG. 6

A drawing to illustrate the aggregation and coalescence of chylomicrons on partial destruction of their protein films.

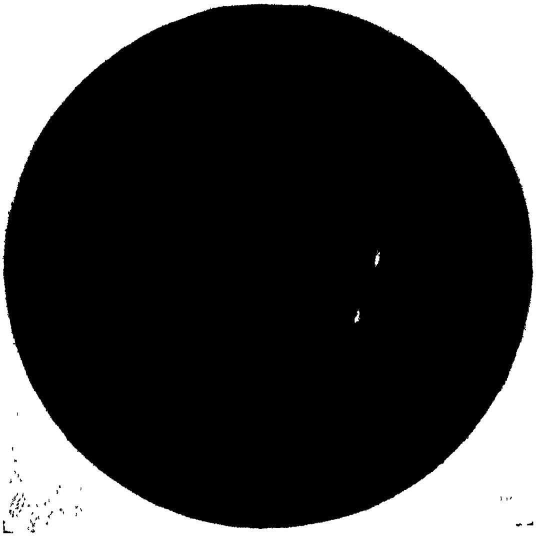

FIG. 7

A photomicrograph showing fat drops which resulted from the coalescence of chylomicrons on treatment of blood serum with an equal volume of normal hydrochloric acid. (Dark-field microscope with oil immersion objective.).

the accompanying drawings. Figure 5 represents isoelectric aggregation and Fig. 6 aggregation with coalescence. They are by no means accurate pictures of the two, but convey the idea of the difference between them better than photomicrographs which have been secured up to the present time.

Large lipoid-looking drops frequently accompanied the coalesced aggregates and there was a decided tendency for them to appear when the preparations stood overnight. The combined coalescence and aggregation always occurred with acids just insufficiently strong to cause protein precipitation. The appearance of large lipoid droplets frequently occurred, but did not always do so.

The interpretation given to the phenomenon was the one just suggested, that the protein films around the chylomicrons had been dehydrated with resulting aggregation of the chylomicrons accompanied by more or less coalescence due to the cracking of the brittle dehydrated films.

If this were the correct interpretation of the phenomenon, it was thought that other substances which precipitate protein should bring about the same result. It was decided to test the hypothesis along these lines. Accordingly equal volumes of serum containing chylomicrons were mixed on microscope slides with different dilutions of 95 per cent alcohol and saturated ammonium sulfate. The mixtures were then covered with cover glasses which were sealed with paraffin. An exceptional procedure was necessary in the case of pure 95 per cent alcohol where two to three volumes to one of serum were required to cause the precipitation of protein. In the case of ammonium sulfate one drop of saturated solution to one of serum brought this about. The preparations were examined in the usual manner using a dark-field microscope with an oil immersion objective.

With strengths of each just insufficient to cause protein precipitation, the same type of aggregation with coalescence was observed as with the corresponding strengths of acid. The coalescence to large lipoid drops did not always occur with ammonium sulfate, although it was definitely observed several times. A beautiful regularly occurring coalescence was, however, observed with alcohol, as described in the following paragraph.

When actual protein precipitation occurred with alcohol, definite small lipoid drops begin to appear floating about among the protein masses very shortly after mixing the serum and alcohol. They gradually increase in size with disappearance of any visible coalesced aggregates. The total volume of droplets was roughly of the order of volume of the free-fat content of a drop of serum. In common with the drops in the other preparations, they were shown to have a higher refractive index than the surrounding medium[29] and thus to be lipoidal by process of elimination.

It has been remarked that the addition of alkali to milk is said to aid the extraction of milk fat with ether, presumably because alkali in proper concentration, destroys the protein films around the fat droplets. Serum containing

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[29] Chamot: "Elementary Chemical Microscopy," John Wiley and Sons, Inc., New York, 230 (1921).

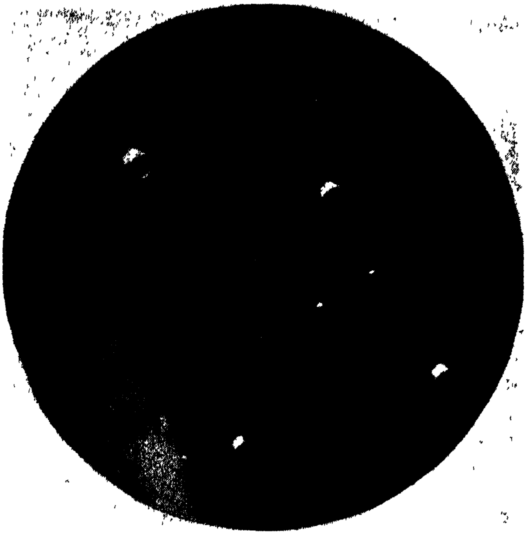

Fig. 8
A photomicrograph showing fat drops which resulted from the coalescence of chylomicrons on treatment of blood serum with an equal volume of sodium hydroxide solution of strength > one per cent. (Dark-field microscope with oil immersion objective.).

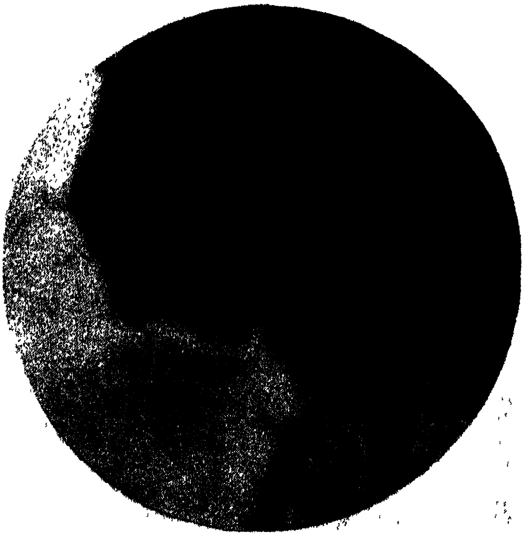

Fig. 9
A photomicrograph showing precipitated protein and fat drops (one in center of picture) which resulted from the coalescence of chylomicrons on treatment of blood serum with two to three volumes of 95 per cent alcohol. (Dark-field microscope with 8 mm objective.)

chylomicrons was accordingly mixed with equal volumes of different strengths of sodium hydroxide solution. With one per cent and more concentrated solution, the formation of coalesced aggregations occurred as regularly as clockwork. Large lipoid drops frequently formed on standing.

Figures 7, 8, and 9 are photomicrographs of fat drops caused by the coalescence of chylomicrons due to the action respectively of normal hydrochloric acid, strong sodium hydroxide solution, and 95 per cent alcohol. In the latter, two small drops are seen in the midst of large masses of precipitated protein. The average diameter of all drops shown was about 4μ.

The behavior of chylomicrons when a protein precipitant or alkali is added to serum is thus in accord with the view that they are normally surrounded by protein films. The experiments afford a picture of the probable coalescence of chylomicrons when large fat globules are formed in storage tissues. In this case the protein films would presumably be destroyed by a proteolytic enzyme.

The Application of the Mudd Interface Technique in Chylomicron Study

The interface technique of Mudd and Mudd[30] has given to workers in pure and applied colloid chemistry a most useful research method and to teachers of the subject a splendid method of demonstration. With such a technique available for the investigation of surface properties the authors could not feel satisfied until an attempt had been made to apply it in the present problem.

As ordinarily employed, a drop of solution containing the particles to be investigated is placed on a microscope slide with a drop of a suitable oil. A coverglass is placed over the two in such a manner that the oil spreads under the glass driving the water phase before it. The slowly advancing oil-water interface, appearing as a bright line, is followed by observation with the dark-field microscope.

The behavior of particles or groups of particles when struck by the interface yields most interesting and important information as to the nature of their surfaces and often as to their consistency, structure, and mode of aggregation.[31] Non-acid-fast bacteria are not readily wet by oil and resist passage into the advancing oil phase. Acid-fast bacteria, on the other hand, have lipoid-like surfaces. They are readily wet by the oil, and consequently readily pass into it. Clumps of bacteria may be entirely dispersed by the interfacial forces.

To the time of writing it has only been possible to examine the behavior of isoelectric aggregations of chylomicrons when struck by an advancing film of triolein. These clumps were formed in the usual manner and the serum containing them then diluted from one to fifty times with a pH 5.0 acetate buffer solution. Generally the whole aggregate seemed to "explode" into the oil, that is, the advancing phase simply dissolved the constituent chylomicrons. Occasionally the clumps were dispersed into constituent smaller clumps or single chylomicrons and spread along the interface, either traveling along it until out of the field of view or "exploding" individually into the oil.

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[30] J. Exptl. Med., **40**, 633, 647 (1924).

[31] Seifriz: Alexander's "Colloid Chemistry," **2**, 437 (1928).

In the first place the "explosion" of the chylomicrons into the oil affords a beautiful visual demonstration of their fatty constitution. The dispersion of aggregates is a most interesting structural phenomenon. The temporary stability of single particles in the interface, observed in some cases, indicates the presence of protective films which are, or course, here also indicated by the fact that the original clumped particles do not coalesce to form one large drop.

The "explosion" of the majority of the isoelectric aggregates immediately upon being touched by the oil might appear to be evidence against the existence of protein films in those cases. However, milk-fat drops which are known to be surrounded by protein films, are also known to show somewhat similar behavior.[32] The authors diluted cream with 200 volumes of pH 4.6 acetate buffer solution to bring the fat droplets to the isoelectric point[33] of their "casein" films. Drops of the mixture were then examined with the interface reaction. In all observed cases the fat drops "exploded" immediately upon being struck by the interface. It would appear that the interfacial forces are sufficient to destroy films of isoelectric protein on fat drops. It may therefore be said that results obtained to date in the application of the Mudd interface technique to the study of chylomircons are entirely in accord with the view that the chylomicrons are surrounded by protein films.

The foregoing results together with certain observations of Mudd and Mudd[34] on the action of the interface on single particles in blood and serum indicate that the application of the interface technique in chylomicron study should be continued.

Summary

The blood transports food fat as an emulsion of minute droplets called chylomicrons.

As emulsion particles the chylomicrons should presumably be surrounded by protective surface films. Preliminary considerations show the examinaton of these films to be the next logical step in the study of the chylomicron emulsion, and of probable importance in special physiological and pathological problems.

Consideration of the nature of the chylomicrons and the composition of blood serum strongly suggests that the films around the chylomicrons consist of protein.

The pH of the isoelectric point of the chylomicrons in human serum has been determined both by a maximum flocculation and a cataphoretic method. In all cases the value lay between pH 4.6 and 5.4, and definitely between the accepted values for the isoelectric points of serum albumin and serum globulin. The more exact cataphoretic method indicates that the isoelectric point lies between pH 4.8 and pH 5.0. In this connection it is most interesting and significant that Abramson[35] has recently shown that quartz particles and paraffin oil droplets both have isoelectric points between pH 4.7 and pH 4.8 in 1150 serum dilutions, very close to the above values for the chylomicrons, as would be expected.

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[32] A personal communication from Dr. Stuart Mudd. The authors take this opportunity to express their appreciation of Dr. Mudd's interest in this problem and for advice which he has given in connection with the cataphoresis and the interface-technique experiments

[33] Michaelis and Pechstein: Biochem Z., **47**, 260 (1912).

[34] J. Exptl. Med., **43**, 127 (1926).

The fact that the isoelectric point of the chylomicrons is thus definitely within the range of the isoelectric points of the proteins, is probably the best evidence that can be brought to prove the hypothesis that they are surrounded by protein films.[17,36]

The position of the isoelectric point between those of the principal serum proteins leads to the interesting hypothesis that the surface films may be composed of mixed serum albumin and serum globulin.

In checking the values reported here and in extending the results to human plasma and to the plasma and serum of animals, the cataphoretic method is strongly recommended. The results are more exact and clearcut, than is the case with the maximum flocculation method, and the technique is less complicated and requires much less time and effort. The isoelectric precipitation of globulin sometimes interferes with the maximum flocculation method, presumably when the serum is too much diluted with acid.

The isoelectric point results lead to the hypothesis that protein precipitants and alkali, which would be expected to dehydrate or otherwise destroy protein films, should cause aggregation and coalescence of chylomicrons. Experiments with strong acid, alkali, 95 per cent alcohol and ammonium sulfate have confirmed this hypothesis and thus afford important independent evidence of the existence of protein films on chylomicrons.

Results obtained to date in the application of the Mudd interface technique to the study of chylomicrons are in accord with the view that the chylomicrons are lipoid droplets surrounded by protein films.

The general conclusion is that the chylomicrons are surrounded by protein films. This fact is of the utmost importance in the act of transport of food fat by the blood. It is further of possibly great importance in the assimilation of fat from the blood and its storage and final utilization. Finally, any knowledge of the surface films on these naturally occurring lipoid droplets in blood serum may be of value in clinical procedures such as precipitation tests for syphilis, in which suspensions of foreign lipoid droplets are added to it.

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The Department of Industrial Research,
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Philadelphia, Pennsylvania.

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[35] Abramson: J. Gen. Physiol., **13**, 177 (1929).

[36] In this connection see Abramson: Colloid Symposium Monograph, **6**, 115 (1928); J. Gen. Physiol., **13**, 169 (1929); Clayton, "Theory of Emulsions," P. Blakiston's Son and Co., Philadelphia, 88 (1928).

THE INFLUENCE OF SIZE, SHAPE, AND CONDUCTIVITY ON CATAPHORETIC MOBILITY, AND ITS BIOLOGICAL SIGNIFICANCE. A REVIEW

BY HAROLD A. ABRAMSON

I. The Cataphoresis of Sub-microscopic and Microscopic Particles

Introduction. The characterization of the surfaces of microscopically visible particles by means of electrical mobility measurements is achieving more importance with the development of methods designed to measure accurately cataphoretic mobilities and streaming potentials. Thus the electrokinetic properties of cellulose particles, latex particles, oil droplets, blood cells, bacteria, inert surfaces covered more or less completely with proteins, protein particles, particles of clay and of fine metal wires have been of particular interest to the physicist, the chemist, and the biologist (Fig. 1). Indeed, the general chemical composition of the surfaces of particles suspended in liquids can be approached most satisfactorily by the study of electrokinetic phenomena.

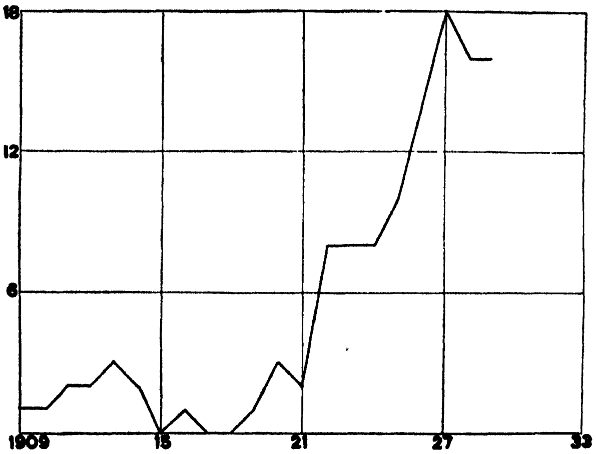

FIG. 1

The abscissa is marked off in years from 1909 to 1930. The ordinate values are the number of the references given under the heading *cataphoresis* in the yearly index of Chemical Abstracts during this period. This chart indicates the general increase in the number of investigations dealing with electrokinetic phenomena.

Before satisfactory conclusions can be drawn, however, regarding the chemical composition of the surfaces of microscopic particles suspended in liquids, the influence of the size, shape, and conductivity of the particle on electrical mobility must be ascertained. It is the purpose of this communication to review data relative to these questions which the author has obtained or considered since the Symposium of 1928. Certain problems then presented are here brought to a more satisfactory solution.[1]

Theoretical. According to the theory developed first by von Helmholtz and subsequently extended by Lamb, Perrin, Pellat, and von Smoluchowski, the equation for V_p, the cataphoretic velocity of a particle relative to a given medium is

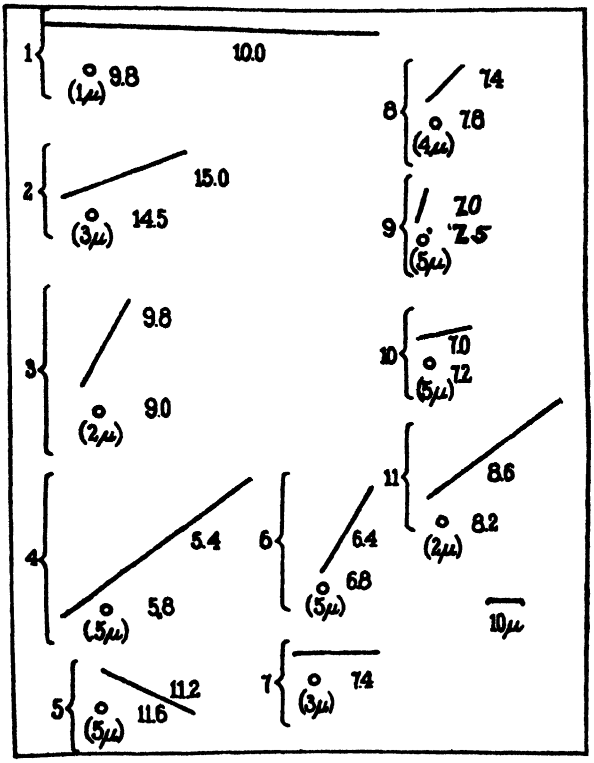

FIG. 2

The brackets indicate needles and globules studied in pairs. Nos. 1-3 are m-aminobenzoic acid crystals and mastic globules covered with gelatin. Nos. 4-10 are asbestos needles and paraffin oil globules covered with egg albumin. No. 11 is a m-aminobenzoic acid crystal and a paraffin oil globule covered with gelatin. The oil globule and mastic particles are all drawn the same size but their diameters are given in parentheses near the particle. The needles were drawn to the scale in the lower right hand corner. Each pair was studied at the same level in the cell. The numbers following each particle are the relative speeds. It is evident that when particles which vary as widely as these in size and shape have similar protein surfaces, there is no difference in cataphoretic velocity. (From the Journal of General Physiology).

$$V_p = 1/4\pi \frac{XD\zeta}{\eta} = C\frac{XD\zeta}{\eta} \qquad (1)$$

(X = field strength; D = dielectric constant of the medium; ζ = electrokinetic potential; η = viscosity of the medium; all units c.g.s. electrostatic.)

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[1] Abramson: Colloid Symposium Monograph, 6, 115 (1928).

Equation (1) predicts that: (a) cataphoretic mobility should be independent of the size and shape of the particle, and (b) for similar surfaces (ion atmospheres), V_E, the electroendosmotic velocity of a liquid past the flat surface, should be equal to V_D, the velocity of the particle relative to the liquid.

Debye and Hückel,[2] on the other hand, have maintained on theoretical grounds that the constant, $1/4\pi$, in equation (1) was valid only for the cataphoresis of cylindrical particles. For spherical particles the factor $1/6\pi$ was substituted. In other words, according to this theory, the constant, C, in equation (1) is dependent upon the shape of the particle.

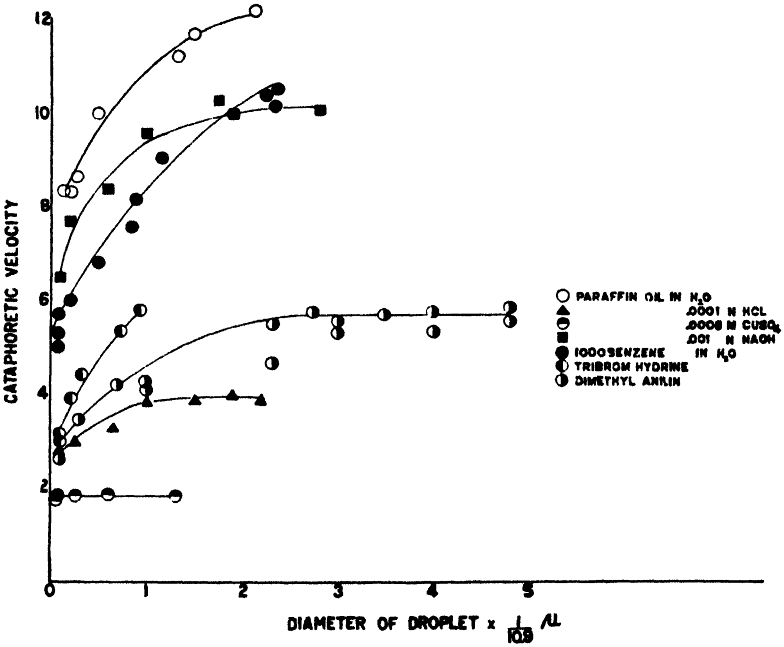

Fig. 3
Data of Mooney. Relative cataphoretic mobilities of the droplets of various emulsions in water and dilute electrolytes.

The Influence of Size and Shape of Particle on Cataphoretic Mobility. Table I summarizes the types of particles and the experiments in which the electrical mobility of the particle has been found to be independent of size and shape. The data there assembled are particularly striking if one recalls that the velocity of a spherical particle moving in a liquid in a gravitational field is proportional to the *square of the radius* and that the frictional resistance encountered by an uncharged spherical particle moving in a liquid is proportional *to the radius*. Fig. 2 illustrates a striking experiment comparing the mobilities of small spheres and very long cylinders.

Of particular importance in the conduct of experiments designed to study the influence of size and shape on electrical mobility is the technic that has

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[2] Physik. Z., 25, 49 (1924).

TABLE I

A Summary of Particles that have Cataphoretic Mobilities independent of Size and Shape as determined by Experiment

Kind of Particle	Size Range (approximate)	Migration Velocity Independent of	Medium	Authority
Protein Sols	Differed submicroscopically	Size	Acetic Acid	Hardy[3]
Silver Sols	Differed submicroscopically	Size	Water	Burton[4]
Gas Bubbles	60μ to 160μ	Size	Water: Electrolytes	McTaggart[5]
Paraffin Oil Droplets	18μ to 28μ	Size	0.001 M NaOH	Mooney[6]
	33μ to 44μ	Size	0.0001 M NaOH	
	1μ to 16μ	Size	0.0008 M $CuSO_4$	
	16μ to 24μ		0.0001 M HCl	
Dimethyl Aniline Droplets	33μ to 50μ	Size	Water	Mooney[6]
Polymorphonuclear Leucocytes and their Aggregates	5μ to 10μ	Size and Shape	Serum; Plasma	Freundlich and Abramson[7]
Blood Platelets and their Aggregates	2μ to 15μ	Size and Shape	Plasma	Abramson[8]
Single Red Cells and their Aggregates	4μ to 30μ	Size and Shape	Serum	Freundlich and Abramson[7]
Air Bubbles in Gelatin Gels	2μ to 50μ	Size	Dilute Electrolytes	
Quartz, Glass, Clay	3μ to 15μ	Size and Shape	Dilute Electrolytes	Abramson[9]
			Distilled Water Sugar Solutions	Freundlich and Abramson[7]
Nujol	0.5μ to 30μ	Size	Water-Ethyl Alcohol and Phosphate Buffer	Abramson and Michaelis[10]
Castor Oil	1μ to 10μ	Size		
Benzyl Alcohol	1μ to 45μ	Size	HCl Solution and Gelatin	
Cocoa Butter	1μ to 8μ	Size		
Nujol	1μ to 25μ	Size	HCl Solution and Gelatin	Abramson[10],[11]

TABLE I (Continued)

A Summary of Particles that have Cataphoretic Mobilities independent of Size and Shape as determined by Experiment

Kind of Particle	Size Range (approximate)	Migration Velocity Independent of	Medium	Authority
Asbestos Needles	5μ to 50μ	Length	Distilled Water	Abramson and Michaelis[10]
Tyrosine Needles	2μ to 100μ	Length	Dilute HCl	Abramson[11]
Dissolved Crystallized Egg Albumin	5×10^{-7} cm (approx.)	This protein has been studied by these investigators in N/50 acetate buffer from pH 3.6 to 5.4 The mobilities of all three kinds of particles of egg albumin are very nearly alike.		Svedberg and Tiselius[12]
Gold Particles covered with Crystalline Egg Albumin	5×10^{-6} cm (approx.)			Prideaux and Howitt[13]
Quartz Particles covered with Crystalline Egg Albumin	0.5μ to 10μ			Abramson[11]
Paraffin Oil	1μ to 5μ (droplets)	When these particles which vary widely in size and shape are covered with gelatin, electrical mobility is independent of size and shape. See Fig. 2.		Abramson and Michaelis[10]
Asbestos Needles				
m-Amino-Benzoic Acid Needles	12μ to 150μ (needles)			

[3] J. Physiol., **29**, xxvi (1903).

[4] "Physical Properties of Colloidal Systems," 2nd ed., 144 (1921).

[5] Phil. Mag., **27**, 297 (1914).

[6] Phys. Rev., **23**, 396 (1924).

[7] Z. physik. Chem., **128**, 25 (1927); **133**, 51 (1928).

[8] J. Exptl. Med., **41**, 445 (1925); **48**, 677 (1928).

[9] J. Am. Chem. Soc., **50**, 390 (1928).

[10] J. Gen. Physiol., **12**, 587 (1929).

[11] Unpublished data.

[12] J. Am. Chem. Soc., **48**, 2272 (1926).

[13] Proc. Roy. Soc., **126**, A, 126 (1929).

been developed to insure chemical uniformity of surface. In the case of solid particles like quartz, glass particles, asbestos needles, and tyrosine needles electrical mobility is independent of size and shape in the size range indicated[14] regardless of the medium. Emulsions behave differently. Mooney[6] found that the migration of paraffin oil droplets increased with increasing radius. The addition of a trace of gelatin or other protein which is adsorbed by the droplets to these systems gives all the droplets, regardless of size, the same migration velocity. The gelatin, in all probability, gives the oil droplets similar surfaces. That in these instances the protein surfaces behave during cataphoresis very much like the dissolved protein has been pointed out previously. This point will be amplified further on.

Electrolytes have the same effect as the proteins, for in their presence the differences between large and small oil droplets become less or disappear.

The Cataphoretic Mobility of Oil Droplets. Figure 3 summarizes the data Mooney has obtained for the cataphoretic velocities of the droplets of various emulsions. The electrical mobility, as Fig. 3 demonstrates, increases with increase in radius. It seems likely that this variation in mobility with size must be related to changes in surface rather than to a purely frictional phenomenon. Even though it has been shown in the previous section that mobility is independent of size and shape for certain microscopically visible particles, and even though there does not seem to be an easily measureable difference between dissolved protein of radius about 10^{-6} cm and adsorbed protein of particle radius to about 10^{-2} cm this can by no means be extended to all particles below the size range investigated in particular.

The meaning of the differences in behavior between the particles listed in Table I and the oil droplets investigated by Mooney has been discussed with Professor H. Müller of the Massachusetts Institute of Technology. Before our discussion with Professor Müller we had believed that the differences were primarily due to a variation in charge density, σ, with curvature of the surface of the droplets. This viewpoint is discussed in section 2 below. Professor Müller has contributed the viewpoint presented in section A following. It is with much pleasure that we are able to incorporate his treatment here.

A.[15] According to Debye and Hückel[16] the cataphoretic velocity of a colloidal particle of spherical form is

$$V_p = \frac{1}{6\pi}\,\frac{XD\zeta}{\eta} \qquad (2)$$

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[14] Tyrosine particles less than 2μ in length may move more slowly than the larger needles, according to the results of a preliminary investigation. If one could obtain tyrosine needles smaller than 2μ, but still perfectly formed crystals, it seems likely that the mobility of these small needles would be like that of the larger ones. Pulverization of a crystal changes the surface energy and consequently, also, the ions adsorbed. It would be of interest to study the solubility of finely pulverized tyrosine. The amphoteric nature of this substance may lead to an unusual increase in solubility.

[15] Section A is a personal communication from Müller, Massachusetts Institute of Technology, May 28, 1930.

[16] Physik. Z., 25, 49 (1924); Hückel: 25, 205 (1924).

To explain the observed variation of the mobility with the radius we note that in this formula only the electrokinetic potential, ζ, may depend on the radius. This potential is due to the electric double-layer around the particle. It therefore depends on the charge density, σ, *i.e.*, the electric charge per cm,^{2}. and on λ, the thickness of the double layer. If we consider the double layer as a rigid system in the sense of a Helmholtz double layer, we would have

$$\zeta = \frac{4\pi\sigma}{D}\lambda. \tag{3}$$

There are consequently two possibilities to explain the observed variation in cataphoretic velocity according to this formulation. It may be due to a dependence of σ or of λ on the curvature of the surface.

In fact we can show that either quantity may be responsible for the observed variation.

1. Dependence of the thickness of the double layer on the radius of the particles.

According to Gouy,[17] Debye and Hückel, etc. we must assume that the electrical double layer is not rigid, but that the outer layer is "diffuse," *i.e.*, it is formed by those ions in the solvent which are electrostatically attracted to the surface. Debye shows that within this ionic atmosphere the potential, φ, decreases with the distance, r, from the center of the ion as

$$\varphi = K\frac{e^{-\kappa r}}{r}, \tag{4}$$

where

$$\kappa^2 = \frac{4\pi N\epsilon^2}{1000\,D\,k\,T}\Sigma\,\gamma_i\,z_i^2$$

N = Avogadro's number; ϵ = electronic charge; k = Boltzmann constant: γ = concentration of ions of the "ith" type in mol/liter having valence of the "zth" type.

For water at 0°C

$$\kappa = 0.229\sqrt{\Gamma}\cdot 10^8\ \mathrm{cm}^{-1} \tag{5}$$

$\Gamma = \Sigma\,\gamma_i\,z_i^2$ = ionic strength of the electrolyte.

The constant K depends on the density of the adsorbed charges and is determined by the condition that on the surface $r = R$. (R = radius of particles)

$$\left(\frac{d\varphi}{dr}\right)_{r=R} = -\frac{4\pi\sigma}{D}. \tag{6}$$

The electrokinetic potential is the value of φ on the surface, hence

$$\zeta = K\frac{e^{-\kappa R}}{R}. \tag{7}$$

Differentiating φ and introducing in (6) gives

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[17] J. Phys., (4) 9, 457 (1910); Ann. Phys., 53, 239 (1917).

$$\zeta = \frac{4\pi\sigma}{D} \cdot \frac{1}{\kappa} \cdot \frac{\kappa R}{1+\kappa R}. \tag{8}$$

Comparison with (3) shows that this diffuse double layer is equivalent to a rigid double layer of the thickness

$$\lambda = \frac{1}{\kappa} \cdot \frac{\kappa R}{1+\kappa R}. \tag{9}$$

This formula shows that, in general, the thickness of the double layer depends on the radius R of the particle. This dependence can, however, be neglected if $\kappa R >> 1$ for then $\lambda = 1/\kappa$, approximately. The dependence of λ on R will only manifest itself if κR is small. In order to find how small R has to be in order to produce any effect we plot in Fig. 3a the function $f(\kappa R) = \kappa R/1 + \kappa R$.

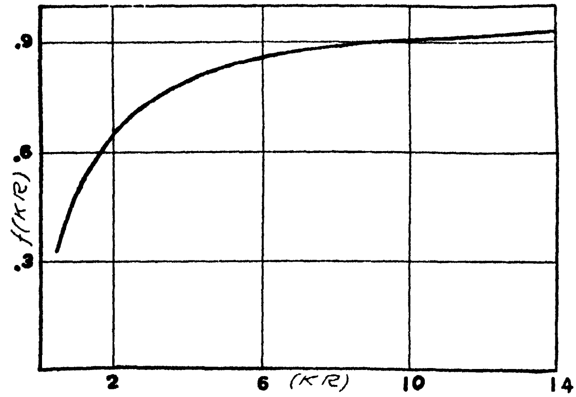

FIG. 3a
See text for explanation of this figure.

This diagram shows that the thickness of the double layer shows an observable variation with size of the particle only if

$$\kappa R \leqq 5$$

or if

$$R \leqq \frac{5}{\kappa} = \frac{2.2}{\sqrt{\Gamma}} 10^{-7} \text{ cm} \tag{10}$$

(for particle in water at 0°C).

Qualitatively, this theory gives, indeed a decrease of the thickness of the double layer, and hence also a decrease of the potential, ζ, and of the mobility, V_p, with decreasing radius of the particle. This is in good agreement with the observed facts. The theory also accounts for the fact that with an addition of any electrolyte the size-effect is shifted to smaller radii or disappears in the range investigated. An addition of electrolyte increases the ionic strength, Γ, hence according to equation (10) the radius, R, has to be correspondingly smaller to produce any variation.

Quantitatively however, the theory does not check very well. According to equation (10) the concentration of the electrolyte would have to be smaller than one micromol/liter in order to produce a measurable effect for particles of microscopic size ($1\mu - 10\mu$) while the effect is observed on even larger particles in solutions with probably stronger concentrations.

If the effect were due to the variation of the thickness of the double layer, it would only depend on the concentration of the electrolyte and not on the character of substance on the surface of the particle. Since the experiments indicate that the surface material is an important factor for the existence of the effect, it is more probable to find the reason for its existence in the dependence of the surface density, σ, on the curvature of the surface. (This is the end of Professor Müllers communication).

2. Dependence of the adsorbed charge density on the radius of the particle.

It is well known that the vapor pressure of very small liquid droplets is greater than the vapor pressure of large ones. The thermodynamic relationship between the vapor pressure of droplets and their radii has been given by Thomson[18]

$$\frac{RT}{M}\ln\frac{p_2}{p_1} = \frac{2S}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \qquad (11)$$

(R = gas constant; T = absolute temperature; M = molecular weight of the liquid; S = the surface energy (interfacial energy); ρ = density of the liquid; p = vapor pressure of the droplet; r = radius of the droplet.)

In equation (11) S is unknown and may be influenced by the differences in adsorption by droplets of different sizes and by the change in charge incidental to this adsorption. Similarly the vapor pressure of the liquid drops of different radii is also unknown. It is apparent, however, that the smaller droplets and solid particles can have higher vapor pressures (solubility) than the larger ones. If the adsorption of ions decreases with increasing vapor pressure, the decrease in velocity of the smaller droplets can be explained at least qualitatively as follows. If we assume S to remain constant for droplets of different radii in solutions of the same ionic strength, and the velocity of the droplet to vary inversely proportional to its vapor pressure, then, we may state,

$$\frac{RT}{M}\ln\frac{V_1}{V_2} = \frac{2S}{\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

approximately.

It seems likely from Mooney's data that large droplets approach a limiting value, V. In that case $r_1 \rightarrow \infty$ and $V_1 \rightarrow V$. We would then have

$$\frac{RT}{M}\ln\frac{V}{V_2} = \frac{2S}{\rho r_2}. \qquad (12)$$

Since Mooney's data are qualitative the validity of equations (12) can not as yet be exactly tested. From (12) it follows that

$$-\ln V_2 \propto 1/r_2.$$

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[18] Cited by H. Freundlich: Colloid Chemistry, p. 45 (1926).

TABLE II

The Bulk Conductivity of Microscopic Particles covered with Protein Films does not influence their Cataphoretic Mobility

Particle	Time to migrate given distance sec.	Medium
B*	9.4	N/100 HCl plus a trace of gelatin
Q	9.0	
Q	9.4	
B	9.0	
Q	8.8	
Q	9.6	
B	9.2	
Q	9.4	
B	9.1	
P	6.4	In equilibrium with N/50 Acetate Buffer and trace of gelatin
A	6.4	
A	6.4	
A	6.6	
P	6.7	
A	7.0	
A	6.8	
A	6.5	HCl plus trace of hemocyanine
A	6.4	
A	6.8	
P	7.2	
A	7.0	
A	7.0	
P	7.8	N/100 HCl plus trace of gelatin
A	7.0	
A	7.0	
P	6.0	
C	6.0	
P	5.8	
C	5.8	
P	4.5	
C	4.8	

* B = benzyl alcohol, Q = quartz, A = agar particles in equilibrium with medium, P = paraffin oil, C = carbon.

That is, the negative logarithm of the droplet velocity should be inversely proportional to the radius of the droplet.

The proteins studied, as mentioned previously, hardly change their mobilities when the radii of the particle range[19] from approximately 10^{-6} cm to 10^{-3} cm. These substances acquire their charge in the systems studied not primarily by adsorption of ions but most probably by a stoichimetrical reaction. They possibly represent a special case. And it may be anticipated that when solid particles of pulverized quartz or tyrosine needles are investigated in the ultramicroscopic region, differences in mobility incidental to diminution in radii may be encountered. It is doubtful if the analogy with oil droplets is altogether strict. The pulverization of crystals produces changes in interfacial energy because of changes in the type of crystal surface made available to the solvent. What difference in mobility would exist between perfectly formed tyrosine needles 100μ and 0.01μ in length is unknown.

The influence of the bulk conductivity on cataphoretic mobility. Equation (1) is only strictly applicable to particles that are insulators. Particles homogeneous as a whole cannot be compared in order to study the effect of the conductivity of the particle on electrical mobility for the specific conductivity of the particle cannot be changed with varying the chemical composition of the phase boundary. Particles having identical surface films but varying in the specific conductivity of the enclosed bulk can be obtained by suspending various particles in dilute protein solutions. Table II summarizes experiments performed with Michaelis.[10] Particles of about the same size of quartz, paraffin oil, benzyl alcohol, carbon, and swollen agar covered with protein films, as indicated in the table, migrate independent of the bulk conductivity of the particle. In Table I the electrical mobilities of dissolved egg albumin, of submicroscopic gold particles, and of microscopic quartz particles covered with the same protein are similarly seen to be apparently unaffected by the bulk conductivity of the particle. Zakrzewski[20] has observed in a somewhat different type of experiment, however, that the streaming potentials set up in silvered glass capillaries are a function of increasing thickness of the silver film. The conditions of Zakrzewski's experiments are somewhat different from ours. But they emphasize that a good deal of similar experimentation is necessary before the problems dealing with bulk conductivity and electrokinetic phenomena are solved.

The Factor of Proportionality for Cataphoretic and Electroendosmotic Mobilities[21]

Theoretical. The data presented in the foregoing sections make it likely that microscopic particles having identical surfaces migrate independent of size and shape. This is, as previously stated, contradictory to the theory postulating that the factor C in equation (1) is a function of the shape of the particle. While these experiments deal with rather extreme variations of size and shape they are not definitely a test of that boundary condition of Debye and Hückel's theory which assumes that the radius of curvature of the cylinder is very large in comparison with the thickness of the ion atmosphere.

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[19] It will be shown in the next section that the range of radii of curvature over which a given protein does not change its mobility is from about 10^{-6} cm to 10^{a} cm where $a \rightarrow \infty$.

[20] Physik. Z., **2**, 146 (1900).

[21] This section has since appeared in J. Gen. Physiol., **13**, 657 (1930).

An experimental investigation including a test of the boundary condition involves the measurement of cataphoretic mobility of particles in a given medium simultaneously with the electroendosmotic mobility of the medium relative to a flat surface[22] having an ion atmosphere identical with that of the particle. Substituting the values of Debye and Hückel[2] for C in equation (1) and solving for R, the ratio of E_E and V_p, we obtain

$$R = V_E/V_P = 1.5$$

In other words, according to this theory electroendosmotic mobility must be 50 per cent greater than cataphoretic mobility.

Historical. Mooney[6] appears to be the first investigator to attempt to evaluate R. He found that the mobility of oil droplets was independent of size in $CuSO_4$ solutions (Fig. 3). Taking advantage of this fact, Mooney wet the inside of a round capillary tube with a paraffin oil and studied in this system the cataphoretic velocity of the oil droplets and the electroendosmotic velocity of the liquid against a surface presumably covered with oil. In one system V_p was very nearly equal to V_E.

The data of van der Grinten,[23] obtained in a flat cataphoresis cell, are in contrast to the finding of Mooney that $R = 1.0$ (approximately) for a round capillary. Van der Grinten studied the cataphoresis of small glass particles in distilled water, the particles composed of the same glass coverslips from which his flat cataphoresis cell had been assembled. He thus assumed that the surfaces of the particles of glass powder obtained by breaking up his coverslips were the same as that of the flat uninjured coverslips. Van der Grinten interpreted his data to give a mean value of $R = 1.59$, thus apparently confirming fairly well the theory of Debye and Hückel. Abramson[1] powdered pyrex glass and repeated the experiments of van der Grinten with a cell made of the same pyrex glass. This author found that for a given cataphoretic cell, R varied from 1.27 to 3.2 as a function of the nature of the medium. This cell of pyrex glass was not of uniform rectangular cross-section. The values obtained for R were consequently not considered absolute but rather pointing to the fact that a complete reinvestigation of the value of R was necessary under known hydrodynamic conditions and where the flat surface and surface of the particle were chemically identical.

The Movement of Liquids produced by Electroendosmosis in Flat Cataphoresis Cells. The movement of liquids in flat cataphoresis cells has been previously considered adequately for cells of various types by numerous investigators.

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[22] An absolutely flat surface is, of course, not realizable experimentally.

[23] J. Chim. phys., 23, 14 (1916).

Since the recalculations to be made here of certain data depend upon the movement of liquids in cataphoresis cells we shall briefly review the facts pertinent to our subsequent recalculations and investigations.

The theories of Ellis and von Smoluchowski (based upon an old observation of Quincke) have made possible the quantitative measurements of cataphoretic mobility. Ellis assumed that for a closed flat cataphoresis cell of depth x, the observed cataphoretic velocity of a particle was, at any level in the cell, (for a system with no turbulence)

$$V_{obs.} = V_p + V_w \tag{13}$$

(V_p = absolute mobility relative to the liquid due to the charge, constant at all levels; V_w = the velocity of the liquid). The velocity of the liquid, as is well known, may vary from level to level so that if the electroendosmosis be in one direction, the return flow in the midregions of the closed cell must be in the opposite direction in closed systems like those considered. $V_{obs.}$ is, therefore, a function of the liquid streaming. The absolute velocity of a particle is, then, the mean velocity, M, of the particle within the cell,

$$M = 1/x_1 \int_0 V_{obs.}\, dx. \tag{14}$$

Substituting (13) in (14)

$$M = 1/x_1 \int_0^{x_1} (V_p + V_w)\, dx = V_p + 1/x_1 \int^{x_1} V_w\, dx. \tag{15}$$

For a closed cell $1/x_1 \int_0^{x_1} V_w dx = 0$ and since V_p is a constant for a given field strength,

$$M = 1/x_1 \int_0^{x_1} V_{obs.}\, dx = V_p \tag{16}$$

Table III

Recalculation of van der Crinten's Data

Curve No.	$V_{1/5}$ μ/sec.	V_E* μ/sec.	$V_{(3/4\,V_{1/6} + 1/4\,V_{1/2})}$	V_E μ/sec.	$V_{\text{Graphical Integration}}$ μ/sec.	V_E μ/sec.	Mean. R
1 (Fig. III)	2.7	6.6	2.8	6.6	2.8	6.4	2.4
2 (Fig. III)	2.7	6.2	2.8	6.0	2.9	5.8	2.15
3 (Fig. III)	2.7	7.2	3.0	6.6	2.9	6.8	2.4
Fig. 4 Van der Grinten p. 228	2.5	7.2		2.5	7.4	6 8	2.8

* V_E is calculated by means of equation (4).

By measuring V at various levels, V_p may be calculated from the analytic expression relating $V_{obs.}$ to x or V_p is readily obtained by graphical integration.

Von Smoluchowski simplified the method adopted by Ellis by proposing that

$$V_p = \tfrac{3}{4} V_{1/6} + \tfrac{1}{4} V_{1/2} = V_{1/5} = V_{4/5}, \text{ very nearly,} \tag{17}$$

where the small sub-numerals represent level $\left(\text{level} = \frac{\text{depth}}{\text{total depth}}\right)$ in the cataphoresis cell. From the foregoing it can also be readily shown that

$$V_E = 2(V_{1/2} - V_p). \tag{18}$$

(V_E = mobility of the liquid relative to the wall of the cataphoresis cell.) The data of Ellis and of Svedberg and Anderssen have amply confirmed von

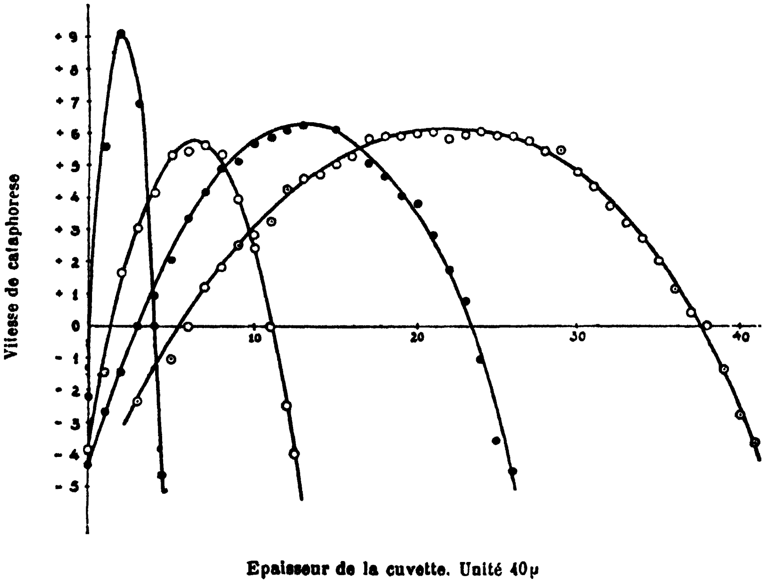

Fig. 4
Data of van der Grinten. (From J. Chim. phys.)

Smoluchowski's theory for the simple type of systems used by Ellis and by Svedberg and Anderssen. Their experiments are in accord with equation (17) in that

$$V_{1/5} = V_{4/5} = V_p = 1/x_1 \int_0^{x_1} V_{obs}\, dx \tag{19}$$

for flat cells from 50μ to about 1.0 mm thick. This means that *in cataphoresis cells of this type and depth the mobility is constant at a given level. And conversely if flat cells of different depths have mobilities in agreement with equations (18) and (19), then the absolute mobilities of the particles measured are governed by equations (18) and (19).* This is of the utmost importance in the recalculation of van der Grinten's data.

Recalculation of van der Grinten's data. It has been mentioned that van der Grinten found R = 1.5, approximately. The data submitted by van der Grinten are of the type given in Fig. 4 which is reproduced from the paper of this author. Curves 1, 2, 3, and 4 in Fig. 4 demonstrate that when van der Grinten's cataphoresis cells were more than 0.52 mm thick, the cataphoretic velocity of the particle (as well as the endosmotic velocity) remained practically constant for the same level in cells of different thicknesses. This does not mean, as van der Grinten interpreted it, that V_P, the speed of the particle relative to the liquid is that found in the midregions of the cells. It is rather, as Table III demonstrates, a further confirmation of the theory of von Smoluchowski. The table gives the values of V_P and V_E calculated by equations (17), (18), and (19) from the curves of Fig. 1 and another curve of van der Grinten's not reproduced here. It is evident that R is much greater than 1.5 in these systems and varies between 2.15 and 2.8. These data so calculated are in agreement with the author's previous experiments where similar high values of R for glass particle-glass surface systems similar to those of van der Grinten's were obtained. If one considers the data submitted by Lachs and Kronman[24] one could postulate *a prioi* that to determine R by means of a flat glass surface and glass particles would be impossible. Lachs and Kronman, after a series of careful streaming potential measurements on glass and quartz surfaces, concluded that no true electrokinetic equilibrium was reached. Furthermore, consideration of the well known sensitiveness to stresses of metal surfaces as determined by measurements of thermodynamic potentials makes it not unlikely that localized changes in surface energy due to pulverization of the glass leads to the high value of R. To determine R, a stable system was here sought where R would be independent of the electrolyte content of the medium, and where, with a reasonable degree of certainty, the particle surface and the flat surface were the same.

The Determination of V_E/V_P *for Flat Surfaces.* It has been shown by Davis,[25] Abramson,[26] and Freundlich and Abramson[27] that surfaces of quartz and glass are practically completely coated with certain proteins when in contact with dilute solutions of these proteins on either side of the isoelectric point,—the particles then acting very much like the native protein in cataphoresis experiments. The most varied substances in addition to quartz and glass coat themselves with gelatin and egg albumin. Thus cystine crystals,[11] menthol,[11] camphor,[11] oil droplets, agar, charcoal, zinc oxide powder and air bubbles behave in this fashion. Briggs[27] has also found that glass capillaries coat themslves with proteins. By suspending glass, quartz and other particles in a protein solution both particles and flat surface of the cataphoresis cell therefore can be coated with the same substance fulfilling the condition of chemical similarity of glass and particle surface.

In the experiments to be reported, R was determined in two different flat cataphoresis cells of uniform cross-section. One of the cells was a cemented cell, similar in arrangement to that described by Northrop[28] and constructed in the fashion previously described.[28] The approximate dimensions of this cell were length 7.0 cm.; thickness 0.1 cm; width 1.0 cm. The second cell, of fused glass, was the modification of the Northrup-Kunitz cell described by Abramson.[29] The approximate dimensions of this cell were: length 3.5 cm; thickness 0.08 cm; width 0.9 cm.[30]

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[24] Ext. Bull. l'acad. Pol. Sci. Lettres (A), 1925, 289.

[25] J. Physiol., 58, xvi (1923).

[26] J. Am. Chem. Soc., 50, 390 (1928); J. Gen. Physiol., 13, 169 (1929).

[27] Briggs has obtained streaming potentials with protein-coated glass capillaries remarkably similar to those obtained by Abramson by the method of cataphoresis. The concentration and kind of electrolyte however differed in these experiments. Until the experiments are repeated under similar conditions of ionic strength and ionic species, *R* cannot be evaluated from these data; J. Am. Chem. Soc., 50, 2358 (1928).

[28] J. Gen. Physiol., 4, 629 (1923).

It has been demonstrated for this type of flat cataphoresis cell that "the movements of the water and particle within the cell follow the theory of von Smoluchowski. . . . When the curve of particle velocity at different levels is parabolic, the curve of velocity as plotted against level is the same near the fused ends of the cell itself as in the middle. The stream lines of the liquid throughout the cell are therefore uniform."[29] The value of R may, therefore, be readily calculated by means of equations (17), (18), and (19).

Table IV gives the value of R for 16 experiments performed with various protein covered particles and the flat glass surfaces of the cataphoresis cells covered with the same proteins. These experiments were performed with two kinds of proteins on both sides of the isoelectric points of the proteins and in

TABLE IV

Experiments to determine R. G. = Fused Glass Cell; C = Cemented Cell

Exp. No.	Cell	Nature of System	V_P μ/sec.	V_E μ/sec.	$R = \frac{V_E}{V_P}$
1	G	Glass of cell, powdered. pH 3.6 N/50 Acetate Buffer + 0.1% Gelatin	11.1	11.8	1.08
2	C	0.004 N HCl Quartz Powder + 0.1% Gelatin	6.4	6.2	0.97
3	G	0.004 N HCl Quartz Powder + 0.1% Gelatin	8.7	8.3	0.95
4	G	Benzyl Alcohol + 0.2% Gelatin	6.0	5.4	0.90
5	G	As above	Data misplaced		0.97
6	G	Powdered Glass in Distilled Water	7.3	20.4	3.3
7	G	Quartz in M/150 pH 7.4 Phosphate Buffer + 1.3% Gelatin	1.23	1.28	1.12
8	C	As above	8.6	7.8	0.91
9	C	As above	9.6	9.1	1.06
10	C	As above but in Acetic Acid	10.0	7.8	0.78
11	C	As above	1.00	9.6	0.96
12	C	As above	10.5	11.4	1.08
13	G	0.1% Egg Albumin Quartz in M/50 Acetic Acid	3.2	3.3	1.06
14	G	As above	10.3	11.8	1.14
15	G	As above but in Phosphate Buffer	8.75	11.1	1.14
16	G	1/3% Gelatin + N/200 H_2SO_4	6.15	5.9	0.96
17	G	As above	12.0	13.9	1.16

For protein coated surfaces (except No. 10) Mn. R = 1.01 ± 0.088. Probable error ± 0.02.

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[29] J. Gen. Physiol., 2, 469 (1928).

[30] The diameter of the side tubes connecting cataphoresis cells and stopcocks were large in comparison with the thickness of the cells themselves.

the presence of different cations and anions. The field strengths were also varied. The values of R for 15 of these experiments varied between 0.90 and 1.16. The sixteenth value was 0.78. The mean (excluding value 0.78) was equal to 1.01 ± 0.088 with the probable error of the mean equal to ±0.02. These data point clearly to the conclusion that, under the given conditions, the ratio of cataphoretic to electroendosmotic velocity is very close to 1.00; and that the factor, C, in equation (1) is the same for V_p and V_E.[31]

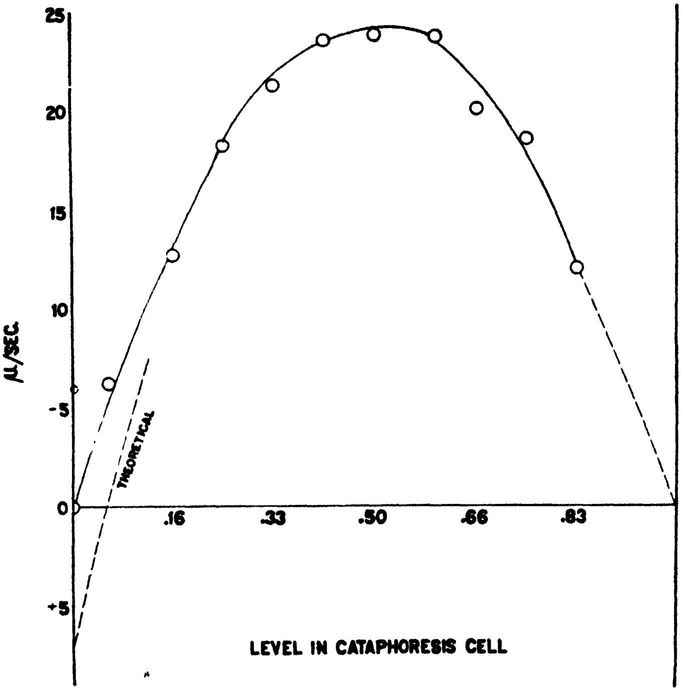

Fig. 5

The smooth curve extrapolated to $x = 1.0$ has been drawn through points of cataphoretic mobility of protein covered oil droplets. The curve passes through the origin. Since the origin ($x = 0$ or 1.0) is the wall of the cell it follows that $V_E = V_p$, or $\frac{V_E}{V_p} = 1.00$ approximately. The dotted line gives an idea of how the curve would look if $\frac{V_E}{V_p}$ were equal to 1.50. (From the Journal of General Physiology).

The Determination of V_E/V_p for a Round Surface. By proceeding as in the preceding section, V_E/V_p was determined in a round microcataphoresis cell by coating particle and glass surface with a protein, here gelatin. The curve drawn through the points in Fig. 5 is typical of the data of four similar experiments. The absolute mobility of the protein covered particle, V_p, is here at the level 0.15, approximately. The curve passes through the origin. This is only possible when

$$V_E = V_p \text{ or } V_E / V_p = 1.00$$

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[31] This constant has not been determined experimentally.

The dotted line in Fig. 5 follows the approximate course of the curve calculated on the assumption that $V_E/V_P = 1.5$. That this ratio does not obtain under these conditions is obvious, confirming, therefore, the data for flat cells.

Significance of Data for Biological Objects

The Cataphoretic Mobility of Mammalian Red Blood Cells. Until more is known of the laws governing the cataphoresis of substances such as those ordinarily isolated from living cells, it is difficult to draw far-reaching conclusions concerning the data at present available dealing with the electrical mobilities of cells. There are, in fact, very few investigations which describe systematically, as *quantitatively* as the methods of cataphoresis permit, the comparative electrical mobilities of microscopic unicellular organisms. However, certain values given for the cataphoresis of mammalian red blood cells are of interest in view of the preceding discussion of the influence of size and shape on electric mobility. The data given in Table V show that very wide differences in the cataphoretic velocity of the red cells of different mammals exist.[32] Further, these values are independent of accidental impurities such as serum, etc. They are actually representative of the physico-chemical make-up of the cell surfaces. But how much justification does there exist for the comparison of these values with one another?

If the surfaces of the cells were composed of protein exclusively, or of substances whose surfaces behaved like tyrosine needles, asbestos, etc., the problem would be simple; for it seems most probable that under such conditions curvature of the surface is not of much significance in determining cataphoretic mobility. Since it is most likely that fatty substances and other more complicated materials are chief components of certain red-cell surfaces, it is evident that curvature of the surface could affect the electric mobility of the red cells in exactly the same way that curvature affects the mobility of the oil droplets.

The following considerations are in favor of the tenability of the viewpoint that the electrical mobilities of the red cells studied are representative of chemical make-up of the surface rather than of variations in curvature of the surface:

a) There is too little known about the cataphoresis of organic substances in different states to accept curvature of the surface as a factor in determining red cell mobilities. The investigation of super-cooled emulsions and solid crystalline compounds of the type investigated by Mooney as well as the constituents of the red cell stroma must first be accomplished.

b) The "ghosts" (stromata) of red blood cells formed by hemolysis with dilute electrolytes can simultaneously be studied with single intact red cells. These hemoglobin-free lipoid portions of red cells undergo during hemolysis important changes in shape and stress incidental to swelling, besides losing their hemoglobin. They have, in consequence, a new shape after hemolysis. The "ghosts" migrate with practically the same speed as normal intact red cells, in phosphate buffer.[11] The same has been found to be true for stroma debris.[33] Changes in curvature do not, therefore, seem to be of primary importance here.

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[32] J. Gen. Physiol., 12, 711 (1929).

c) Salts diminish the differences between droplets of the size of blood cells, particularly in the salt concentrations used.

d) There is no correlation between size and mobility. The diameter of rabbit cells are 7.16μ. Those of the dog are 7.20μ.[34] Yet these two types of cells have the lowest and highest values of mobility, respectively, among the mammals investigated. Similar examples can be cited for other cells of the group.

e) Red blood cells obtained from cases of primary and secondary anemias show very marked changes in size and curvature of the surface.[30] These differences in equivalent radius may be greater than 100 percent in suspensions from one patient. In suspensions from the same patient very little if any

TABLE V

The Cataphoretic Mobility of Mammalian Red Cells at pH 7.35 in M/15 Phosphate Buffer

Order	Animal	mn. μ/sec./volt/cm	Average Deviation
Primate	Man (White)	1.31	±0.02
	Man (Negro)	1.30	±0.05
	Monkey (*Macacus Rhesus*)	1.33	±0.02
Carnivor	Dog	1.65	±0.03
	Cat	1.39	±0.01
Ungulate	Pig	0.98	±0.03
Rodent	Rabbit	0.55	±0.05
	Guinea Pig	1.11	±0.02
	Mouse	1.40	±0.06
	Rat	1.45	±0.02
Edentate	Sloth (Two-toed)	0.97	One series of measurements
Marsupial	Opossum	1.07	±0.02

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[33] One experiment.

[34] Tabulae Biological, Berlin, 2, 459 (1925).

difference is found amongst the cells themselves. The values of mobility obtained for a series of anemia cases did not differ from the normal or differed very slightly, the difference being near the limits of experimental error. The cells, incidentally, also varied in hemoglobin content. This is excellent evidence that size and shape do not primarily invoke changes in red cell mobility.[35,36]

In conclusion we wish to re-emphasize that when data are available for other types of cells, a critique similar to that employed in the foregoing must be applied. The biologist in the meantime must wait upon the further acquisition of values of electrical mobilities of organic compounds in various states and in different suspending media before hoping to understand the chemical make-up of the surface and the many curious phenomena occurring at the phase boundaries of living and non-living microscopic particles and surfaces.

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[35] It is not insinuated that no change in physico-chemical make-up occurs in the red cells in anemia. The changes that do occur cannot profoundly change the constitution of the surface.

[36] Since this paper was written Dr. G. Payling Wright and I have observed that foul red cells which vary in size, shape and cytoplasmic structure may have very much the same electrical mobilities.

STUDIES ON ELECTROKINETIC POTENTIALS. VI

Electrical Phenomena at Interfaces[1]

BY HENRY B. BULL AND ROSS AIKEN GORTNER

Historical and Theoretical

The existence of electrical conductance at a solid-liquid interface which increases the conductance of a system above that normally expected can hardly be doubted since it has been demonstrated by several workers. Thus Stock[2] showed that quartz powder in such liquids as nitrobenzene and aniline greatly increased the apparent conductivities of these liquids. Briggs[3] found that surface conductance must be taken into consideration in determining the specific conductance of a liquid for the purpose of calculating the ζ-potential from streaming-potential data. McBain, Peaker, and King[4] have made accurate quantitative determinations of the surface conductance of KCl solutions at glass and silica interfaces and find it to be appreciable.

Stock[2] at the suggestion of Smoluchowski undertook to investigate the question of surface conductance. He employed in this research certain of Smoluchowski's equations.

Smoluchowski considered a system of capillary tubes and proceeded to calculate the ratio of the current carried by the surface potential, *i.e.*, that due to surface conductance, to that carried by the bulk of the liquid.

The infinitesimal amount of current, dI_s, carried by an infinitesimal element of the double layer moving with a velocity, u, is given by the following relation.

$$dI_s = q\,u\,dS\,dr \qquad \text{(1)}$$

where q is the charge per unit area on the double layer, dS is an infinitesimal section of the circumference, and dr is an infinitesimal normal to the wall.

Then

$$I_s = \int q\,u\,dS\,dr \qquad \text{(2)}$$

But the velocity at any point is given by

$$u = \frac{\partial u}{\partial r} r \qquad \text{(3)}$$

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[1] From the Division of Agricultural Biochemistry, University of Minnesota. Published with the approval of the Director, as Paper No. 951, Journal Series, Minnesota Agricultural Experiment Station. This paper is taken from Part III of a thesis presented by Mr. H. B. Bull to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1930.

[2] Anz. Akad. Wiss. Krakau, (A) **1912**, 635.

[3] J. Phys. Chem., **32**, 641 (1928).

[4] J. Am. Chem. Soc., **51**, 3294 (1929).

Then substituting (3) in (2)

$$I_s = \int q \frac{\partial u}{\partial r} r \, dS \, dr \quad \text{(4)}$$

Integrating part of this expression

$$\int q \, r \, dr = -\frac{1}{4\pi}\int_0^\infty \frac{\partial^2 \phi}{\partial r^2} = \frac{D}{4\pi}(\phi_2 - \phi_1) = \frac{D\zeta}{4\pi} \quad \text{(5)}$$

where $\phi_2 - \phi_1$ is the potential difference across the double layer and is equal to the ζ-potential. D is the dielectric constant.

Substituting (5) in (4)

$$I_s = \frac{D\zeta}{4\pi}\int \frac{\partial u}{\partial r} dS \quad \text{(6)}$$

Integrating through the entire circumference and assuming a linear relation between u and r, we have

$$I_s = \frac{D\zeta}{4\pi} S \frac{u}{d} \quad \text{(7)}$$

where d is the thickness of the double layer.

The movement of the layer of ions with a charge, q, per unit area is produced by an externally applied electrical potential. The resulting force acting on the double layer is

$$F = q \frac{\partial V}{\partial x} \quad \text{(8)}$$

where $\frac{\partial V}{\partial x}$ is the potential gradient of the externally applied electrical potential.

Now at equilibrium the electrical forces tending to produce motion of the liquid must exactly equal the forces tending to retard the flow of the liquid. This resisting force is

$$R = \frac{\partial u}{\partial r} \eta \quad \text{(9)}$$

where η is the coefficient of viscosity. When equilibrium has been reached (9) must equal (8)

$$q \frac{\partial V}{\partial x} = \frac{\partial u}{\partial r} \eta \quad \text{(10)}$$

Assuming a linear relation between u and r, we have

$$\frac{u}{d} \eta = q \frac{\partial V}{\partial x} \quad \text{(11)}$$

where d is the thickness of the double layer.

Substituting the value of u/*d* in (7), we have

$$I_s = \frac{D\zeta S}{4\pi\eta} q \frac{\partial V}{\partial x} \qquad (12)$$

Now the current carried by a cross-section of the liquid is

$$I_A = A\kappa \frac{\partial V}{\partial x} \qquad (13)$$

where A is the area of the cross-section occupied by the liquid and κ is the specific conductance of the liquid.

Dividing (12) by (13)

$$\frac{I_s}{I_A} = \frac{D\zeta Sq}{4\pi\eta\kappa A} \qquad (14)$$

$$\text{Now } q = \frac{\zeta D}{4\pi d} \qquad (15)$$

Substituting (15) in (14)

$$\frac{I_s}{I_A} = \left(\frac{D\zeta}{4\pi}\right)^2 \frac{S}{\eta\kappa A d} \qquad (16)$$

which is the final equation of Smoluchowski.

It is to be noted that in the derivation of this equation the same assumptions are involved which are used in the derivation of the equation for electroosmosis, cataphoresis, and streaming potential. No additional assumptions have been made.

It is possible to modify equation (16) by the appropriate substitution so that two new equations are obtained, one expressing the thickness of the double layer and the other the charge per unit area.

Briggs[5] pointed out that

$$\frac{\kappa_s - \kappa}{\kappa} = \frac{I_s}{I_A} \qquad (17)$$

where κ_s is the specific conductivity of the liquid in the capillary pores and κ is the specific conductivity of the liquid in bulk. $\kappa_s - \kappa$ is taken to be the so-called surface conductance. Then substituting in (16)

$$\frac{\kappa_s - \kappa}{\kappa} = \frac{S}{\kappa A\eta d}\left(\frac{D\zeta}{4\pi}\right)^2 \qquad (18)$$

$$\kappa_s - \kappa = \frac{S}{A\eta d}\left(\frac{D\zeta}{4\pi}\right)^2 \qquad (19)$$

From the streaming potential equation

$$\frac{D\zeta}{4\pi} = \frac{H\eta\kappa_s}{P} \qquad (20)$$

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[5] Colloid Symposium Monograph, **6**, 41 (1928).

Substituting (20) in (19) we have

$$\kappa_s - \kappa = \frac{S}{A\eta d}\left(\frac{H\eta\kappa_s}{P}\right)^2 \quad (21)$$

and

$$d = \frac{S\eta}{(\kappa_s-\kappa)A}\left(\frac{H\kappa_s}{P}\right)^2 \quad (22)$$

which is a convenient equation expressing the thickness of the double layer.

Now substituting the expression $\frac{\zeta D}{4\pi} = d\,q$ in (16) we have

$$\kappa_s - \kappa = \frac{S}{A\eta d}(dq)^2 \quad (23)$$

$$= \frac{S}{A\eta}q^2d \quad (24)$$

Substituting the value of *d* as given by (22), we have

$$\kappa_s - \kappa = \frac{S}{A\eta}q^2\frac{S\eta}{(\kappa_s-\kappa)A}\left(\frac{H\kappa_s}{P}\right)^2 \quad (25)$$

$$= \frac{S^2q^2}{A^2(\kappa_s-\kappa)}\left(\frac{H\kappa_s}{P}\right)^2 \quad (26)$$

or

$$q = (\kappa_s - \kappa)\frac{A}{S}\frac{P}{H\kappa_s} \quad (27)$$

which is an equation expressing the charge per unit area at the interface. The dielectric constant does not appear in either equation for the thickness of the double layer (22) or for the charge (27) which relieves us of making any assumptions concerning the magnitude of this constant.

Now it is not possible in our work with a cellulose diaphragm to determine the actual numerical ratio of A/S in equations (22) and (27), but we can at least assume that *it is a constant for any given diaphragm throughout a series of determinations.* It should be possible therefore to determine the behavior of the charge on and the thickness of the double layer upon the addition of electrolytes by use of the above equations. This is the object of the present research.

The streaming potential apparatus used in this investigation was a modification of that developed by Briggs[3] and later again modified by Martin and Gortner.[6]

The technic is described and the apparatus is figured in diagrams 1 and 2 of the paper by Martin and Gortner.[6]

All volumetric apparatus used in this research was calibrated and the corrections used when necessary.

The quadrant electrometer and potentiometer were adjusted in the usual manner.

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[6] J. Phys. Chem., **34**, 1509 (1930).

The diaphragms used in this research were in all cases made from cellulose. At the beginning of the research, four packages of Schleicher and Schüll filter paper, No. 589, were ground in a ball mill with 95 per cent ethyl alcohol to a pulp. The cellulose was then filtered and dried *in vacuo* at 95° for 8 hours and stored in sealed glass containers. The cellulose was suspended in the liquid to be studied at least 48 hours before it was used.

The cellulose was packed quite tightly in the cell. After the diaphragm was in place in the apparatus, at least 700 cc of the solution to be studied was streamed through it before any determinations were attempted. The washings were discarded.

The two halves of the streaming potential cell were cleaned carefully before each determination with sulfuric acid dichromate solution and rinsed out with distilled water and finally with some of the solution to be used in the experiment.

Determination of the Specific Electrical Conductance of the Liquid in the Diaphragm

Immediately following the determination of the streaming potential, the streaming potential cell was connected to the conductivity apparatus and the resistance of the diaphragm determined.

Later, when the series of experiments on a particular diaphragm was completed, the cell constant of the diaphragm was determined by replacing the liquid in the diaphragm by N/10 KCl. Knowing the cell constant and the resistance, the specific conductivity is calculated in the usual manner.

Calculation of the ζ-Potential

From the observed values of the pressure, the electromotive force, and the specific conductance, the ζ-potential may be calculated. The pressure must be expressed in dynes per square centimeter and the specific conductivity observed in ohms^{-1} must be multiplied by 9×10^{11} to convert it to C.G.S. electrostatic units.

Substituting these conversion factors in the following equations

$$\zeta = \frac{4\pi H \eta \kappa_s}{DP}$$

and collecting constants we have

$$\zeta = 847{,}649{,}000 \, \frac{\eta}{D} \, \frac{H\kappa_s}{P}$$

where H = observed electromotive force in millivolts, η = coefficient of viscosity of the liquid, κ_s = specific conductivity of liquid in diaphragm in ohms^{-1}, D = dielectric constant of liquid, P = pressure in centimeters of mercury, ζ is expressed in millivolts.

In order to determine the surface conductance a conductivity measurement of the liquid in bulk was necessary. This was done at the same temperature as the streaming potential determination and on the liquid which had actually been used in the streaming potential measurements. A Washburn conductivity cell designed for high precision work was used.

The surface conductance was obtained by subtracting the specific conductance of the liquid in bulk from that in the diaphragm.

Chemicals

The water used throughout this investigation was doubly distilled and had a specific conductance of 4.8×10^{-6} ohms^{-1}. It was used fresh.

The salts were the purest obtainable on the market. No additional purification was attempted.

Criteria of Validity Results

It is essential, if we are to attach any meaning to our results, that they must be reproducible. It is to be emphasized, however, that in order to compare results they must have been obtained from material treated in an identical manner. This is particularly true in respect to the time that the cellulose has been allowed to remain in contact with the liquid, since it is generally agreed that the ζ-potential decreases with time when the material is allowed to remain in contact with the liquid. That this is true is clearly shown by the work done by Martin and Gortner[6] and by Lachs and Kronman.[7] The data on three diaphragms with water-cellulose are shown in Table I.

TABLE I

Showing Variability in Streaming Potential Measurements

Diaphragm	Pressure cm Hg	$H\kappa_s/P \times 10^5$	Pressure cm Hg	$H\kappa^s/P \times 10^5$
1	71.9	−10.23	75.9	− 9.85
	75.1	− 9.90	79.1	− 9.70
	78.9	−10.02	72.0	− 9.70
		Average $H\kappa_s/P = -9.90 \times 10^{-5}$		
2	69.0	− 9.48	72.1	− 9.53
	75.5	− 9.48	78.1	− 9.68
	79.8	− 9.45	82.7	− 9.82
		Average $H\kappa_s/P = -9.58 \times 10^{-5}$		
3	65.7	−12.04	73.9	−11.34
	74.5	−11.72	78.1	−11.26
	81.4	−11.67	83.4	−10.97
		Average $H\kappa_s/P = -11.50 \times 10^{-5}$		

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[7] Bull. acad. Polonaise sci. lettres, (A) 1925, 286.

These results were selected purely at random and may be said to represent the usual variations encountered. They perhaps leave something to be desired from the point of view of reproducibility, but when it is remembered that with pure water the observed potential is extremely sensitive to traces of electrolytes and is more erratic than with salt solutions, the disagreement is not serious.

Due to the fact that the gold electrodes are not reversible in the usual sense of the word, it was feared that marked polarization might develop. To satisfy ourselves on this point, we determined the streaming potential as a function of the pressure. The results are shown in Fig. 1.

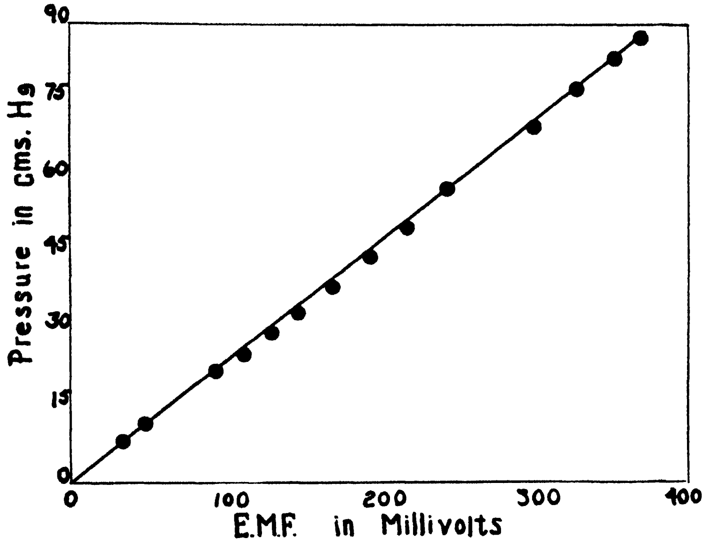

FIG. 1

Showing the relation between the streaming potential and the pressure, as experimentally determined in our apparatus using a cellulose diaphragm and 0.1×10^{-3} NaCl as the liquid being streamed through the diaphragm.

It will be noted that the result is a straight line passing through the origin. Had there been polarization of the electrodes, this would not have been the case.

That the diaphragm had attained equilibrium with the liquid was tested for in every determination by obtaining at least three values while streaming the liquid in one direction and three more values in the reverse direction.

Results

The data for the function, $H\kappa_s/P$, are given in Tables II through IX and summarized along with data for $\frac{\eta}{\kappa_s - \kappa}$ $\left(\frac{H\kappa_s}{P}\right)^2$, $(\kappa_s - \kappa)\frac{P}{\kappa_s H}$, and the ζ-potential in Tables X through XVII and the results graphed in Figs. 2 through 9 for various concentrations of aqueous solutions of KCl, NaCl, $MgCl_2$, $CaCl_2$,

K_2CO_3, K_2SO_4, K_3PO_4, and $ThCl_4$ at a cellulose interface. As a convenience the function, $\frac{\eta}{\kappa_s - \kappa}\left(\frac{(H\kappa_s)}{P}\right)^2$ which is proportional, though not equal, to the thickness of the double layer is designated by d′, and the function, $(\kappa_s - \kappa)\frac{P}{\kappa_s H}$, which is proportional to the electrostatic charge per unit area is designated by q′.

TABLE II

Data for $MgCl_2$

Concentration $MgCl_2$	Pressure cm Hg	$H\kappa_s/P \times 10^5$	Pressure cm Hg	$H\kappa_s/P \times 10^5$
0.00	61.3	−15.5	57.2	−15.5
	78.1	−15.5	79.6	−15.5
	75.5	−15.5	78.3	−15.3
	Average $H\kappa_s/P = -15.48 \times 10^{-5}$			
0.10×10^{-3}	66.3	−10.5	74.5	−11.4
	80.9	−11.1	81.7	−11.1
	73.9	−11.5	75.7	−10.7
	Average $H\kappa/P_s = -11.05 \times 10^{-5}$			
0.20×10^{-3}	51 2	− 8.52	58.9	− 8.84
	80.6	− 9.95	80.6	− 9.42
	78.5	− 9.76	78.9	− 9.45
	Average $H\kappa_s/P = -9.32 \times 10^{-5}$			
0.4×10^{-3}	60.5	− 8.83	63.0	− 8.05
	80.9	− 8.72	81.4	− 8.50
	79.5	− 8.60	79.3	− 8.24
	Average $H\kappa_s/P = -8.50 \times 10^{-5}$			
0.8×10^{-3}	50.1	− 6.90	61.8	− 5.10
	80.6	− 6.94	81.3	− 6.75
	76.5	− 6.68	78.1	− 6.52
	Average $H\kappa_s/P = -6.75 \times 10^{-5}$			
1.6×10^{-3}	81.9	− 2.69	66.9	− 3.10
	80.7	− 2.00	81.1	− 2.71
	Average $H\kappa_s/P = -2.62 \times 10^{-5}$			

TABLE III

Data for CaCl$_2$

Concentration CaCl$_2$	Pressure cm Hg	$H\kappa_s/P \times 10^5$	Pressure cm Hg	$H\kappa_s/P \times 10^5$
0.00	77.2	−13.7	68.3	−13.4
	72.0	−13.8	72.9	−13.6
	69.5	−14.0		
	Average $H\kappa_s/P = -13.7 \times 10^{-5}$			
0.1×10^{-3}	63.5	−10.5	51.8	−11.6
	74.9	−10.4	73.7	−10.5
			78.4	−10.5
	Average $H\kappa_s/P = -10.7 \times 10^{-5}$			
0.2×10^{-3}	53.8	−9.80	57.9	−10.1
	76.9	−9.45	76.9	−9.4
	82.3	−9.20	82.9	−9.3
	Average $H\kappa_s/P = 9.55 \times 10^{-5}$			
0.4×10^{-3}	80.3	−9.2	52.2	−10.8
	82.8	−9.3	73.1	−9.5
	75.5	−9.2	80.4	−9.2
	Average $H\kappa_s/P = -9.55 \times 10^{-5}$			
0.8×10^{-3}	59.0	−10.0	66.0	−9.5
	78.2	−8.9	80.2	−8.5
	83.5	−8.0	82.9	−8.4
	Average $H\kappa_s/P = -8.90 \times 10^{-5}$			
1.6×10^{-3}	70.5	−9.0	67.8	−9.5
	79.0	−8.8	80.3	−8.6
	82.3	−8.7	76.4	−8.6
	Average $H\kappa_s/P = -8.87 \times 10^{-5}$			

TABLE IV

Data for NaCl

Concentration NaCl	Pressure cm Hg	$H_{\kappa_s}/P \times 10^5$	Pressure cm Hg	$H_{\kappa_s}/P \times 10^5$
0.00	71.9	−10.23	75.9	−9.85
	75.1	−9.90	79.1	−9.70
	78.9	−10.02	72.0	−9.70
	Average $H_{\kappa_s}/P = -9.90 \times 10^{-5}$			
0.05×10^{-3}	70.3	−12.80	69.7	−12.84
	78.5	−12.34	74.7	−12.50
	73.9	−12.45	78.6	−12.58
	Average $H_{\kappa_s}/P = -12.6 \times 10^{-5}$			
0.10×10^{-3}	72.9	−13.90	74.1	−14.30
	75.7	−13.85	76.5	−14.40
	79.7	−13.70	73.5	−15.50
	Average $H_{\kappa_s}/P = -14.1 \times 10^{-5}$			
0.2×10^{-3}	71.3	−14.0	72.9	−13.8
	75.1	−13.8	75.9	−13.6
	79.0	−13.7	79.2	−13.6
	Average $H_{\kappa_s}/P = -13.75 \times 10^{-5}$			
0.4×10^{-3}	69.5	−13.4	73.2	−13.3
	74.7	−13.4	76.9	−13.0
	78.3	−13.5	80.2	−13.1
	Average $H_{\kappa_s}/P = -13.30 \times 10^{-5}$			
0.8×10^{-3}	61.5	−12.40	71.7	−11.6
	70.1	−12.45	75.7	−11.6
	77.7	−12.35	82.1	−11.2
	Average $H_{\kappa_s}/P = -11.95 \times 10^{-5}$			
1.6×10^{-3}	67.8	−10.02	75.2	−11.6
	74.8	−10.20	79.4	−11.6
	80.5	−10.25	82.3	−11.8
	Average $H_{\kappa_s}/P = -10.90 \times 10^{-5}$			

TABLE V

Data for KCl

Concentration KCl	Pressure cm Hg	$H_{\kappa_s}/P \times 10^5$	Pressure cm Hg	$H_{\kappa_s}/P \times 10^5$
0.00	51.9	−13.0	51.6	−11.5
	78.4	−12.6	83.0	−12.4
			78.2	−12.6
	Average $H_{\kappa_s}/P = -12.4 \times 10^{-5}$			
0.05×10^{-3}	77.4	−13.8	80.6	−13.8
	82.4	−13.8	77.2	−13.8
	76.0	−13.6		
	Average $H_{\kappa_s}/P = -13.8 \times 10^{-5}$			
0.10×10^{-3}	48.7	−15.1	59.1	−12 4
	82.2	−14.3	77.4	−14.1
	76.1	−14.3	84.4	−14.2
	Average $H_{\kappa_s}/P = -14.01 \times 10^{-5}$			
0.20×10^{-3}	36.7	−13.7	63.3	−13.1
	79.0	−14.3	82.4	−14.2
	85.5	−13.9	78 2	−14.4
	Average $H_{\kappa_s}/P = -13.9 \times 10^{-5}$			
0.4×10^{-3}	81.2	−12.7	50 3	−12.50
	66.8	−12 4	82 9	−12.95
	71.4	−13.5	72.2	−13.40
	Average $H_{\kappa_s}/P = -12.9 \times 10^{-5}$			
0.8×10^{-3}	41.6	−11.75	53.2	−13.7
	76.7	−12.3	76.8	−12.6
	83.3	−12.2	68.7	−13.4
	Average $H_{\kappa_s}/P = -12.8 \times 10^{-5}$			

TABLE VI

Showing Values of H/P for Various Concentrations of K_2CO_3 at a Cellulose Interface

Concentration × 10^3 Normality	Pressure cm Hg	H/P mv/cm	Pressure cm Hg	H/P mv/cm
0.00	65.7	−4.611	73.9	−4.343
	74.5	−4.489	78.1	−4.314
	81.4	−4.471	83.4	−4.202
	Average H/P = −4 405			
0.10	72.2	−3.518	70.6	−3.392
	79.5	−3.515	78.4	−3.475
	84.7	−3.536	83.3	−3.397
	Average H/P = −3.472			
0.20	67.6	−1.819	65.9	−1.904
	81.9	−1.807	81.7	−1.903
	85.1	−1.815	85.4	−1.896
	Average H/P = −1.8573			
0.40	66.6	−1.216	82.1	−1.230
	74.6	−1.206	84.5	−1.207
	83.6	−1.202	87.6	−1.176
	Average H/P = −1.2061			
0.80	75.5	− .7019	76.6	− .6984
	80.9	− .7169	81.3	− .6703
	84.6	− .6973		
	Average H/P = −0.6969			

TABLE VII

Showing Values of H/P for Various Concentrations of K_2SO_4 at a Cellulose Interface

Concentration × 10^3 Normality	Pressure cm Hg	H/P mv/cm	Pressure cm Hg	H/P mv/cm
0.00	69.0	−3.536	72.1	−3.557
	75.5	−3.536	78.5	−3.611
	79.8	−3.527	82.7	−3.663
	Average H/P = −3.5716			
0.10	68.9	−2.721	82.6	−2.451
	82.5	−2.406	85.1	−2.391
	85.3	−2.432	70.7	−2.595
	Average H/P = −2.499			
0.20	80.5	−1.623	80.7	−1.629
	83.1	−1.632	83.5	−1.622
	85.5	−1.674	85.7	−1.621
	Average H/P = −1.633			
0.40	82.7	−0.9068	83.0	−0.9638
	84.2	−0.9086	85.0	−0.9764
	85.9	−0.8789	86.6	−0.9815
	Average H/P = −0.9360			
0.80	76.1	−0.5519	81.5	−0.4969
	81.1	−0.5610	83.9	−0.4946
	85.1	−0.5699	86.3	−0.4866
	Average H/P = −0.5268			

TABLE VIII

Showing Values of H/P for Various Concentrations of K_3PO_4 at a Cellulose Interface

Concentration $\times 10^3$ Normailty	Pressure cm Hg	H/P mv/cm	Pressure cm Hg	H/P mv/cm
0.0	78.0	−2.756	76.5	−2.771
	81.4	−2.751	77.9	−2.766
	84.7	−2.727	80.4	−2.754
	Average H/P = −2 754			
0.1	68.3	−2.554	77.9	−2.734
	76.5	−2.555	71.0	−2.566
	83.7	−2.526	86.1	−2.601
	Average H/P = −2.591			
0.2	84.1	−1.688	75.7	−1.803
	74.6	−1.702	79.2	−1.799
	79.3	−1.683	82.8	−1.793
	Average H/P = −1.744			
0.4	83.4	−1.270	74.4	−1.384
	70.6	−1.288	77.3	−1.384
	77.2	−1.275	79.3	−1.374
	Average H/P = −1.3291			
0.8	71.1	−.6962		
	76.7	−.6844		
	83.1	−.7099		
	Average H/P = −0.6968			

TABLE IX

Data for $ThCl_4$

Concentration × 10^3 Normality	Pressure cm Hg	H/P mv/cm	Pressure cm Hg	H/P mv/cm
0.00	63.1	−5.594	73.6	−5.407
	73.4	−5.585	79.2	−5.290
	80.0	−5.606	83.5	−5.227
	Average H/P = −5.4515			
0.05	72.8	−3.372	75.0	−3.560
	77.8	−3.348	79.2	−3.491
	81.3	−3.327	83.7	−3.453
	Average H/P = −3.4251			
0.10	54.3	−0.9484	65.7	−1.278
	72.0	−0.9097	76.3	−1.238
	79.8	−0.9273	82.2	−1.180
	Average H/P = −1.0803			
0.20	72.3	+1.916	68.3	+2.057
	78.3	+1.948	77.2	+2.014
	81.5	+1.926	82.3	+2.023
	Average H/P = +1.981			
0.40	65.1	+1.590	74.4	+1.660
	71.8	+1.643	79.6	+1.608
	80.2	+1.658	83.6	+1.585
	Average H/P = +1.624			
0.80	56.2	+0.9252	75.2	+0.9973
	74.5	+0.9127	80.0	+1.043
	81.6	+0.9068	84.2	+1.021
	Average H/P = +0.9677			
1.60	68.6	+0.5612	73.3	+0.4570
	78.8	+0.5964	80.0	+0.5250
	82.7	+0.5985	84.2	+0.5403
	Average H/P = +5.464			

TABLE X

Summary of Data for KCl

$$1 = \text{Concentration} \times 10^3;\ 2 = \zeta;\ 3 = \frac{H\kappa_s}{P} \times 10^5;\ 4 = (\kappa_s - \kappa) \times 10^6;$$

$$5 = \eta \times 10^2;\ 6 = \frac{\eta}{\kappa_s - \kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7;\ 7 = (\kappa_s - \kappa)\frac{P}{H\kappa_s} \times 10^{12}$$

1	2 mv	3	4 mhos	5 poise	6	7
0.00	−10.91	−12.4	26.5	0.8	46.37	−21.36
0.05	−12.14	−13.8	34.8	0.8	43.72	−25.23
0.10	−12.37	−14.01	42.4	0.8	37.06	−30.23
0.20	−12.23	−13.9	56.2	0.8	27.51	−40.41
0.40	−11.35	−12.9	67.0	0.8	19.84	−51.92
0.80	−11.26	−12.8	96.0	0.8	13.63	−74.98
1.60	−11.96	−13.6	125.0	0 8	11.84	−91.87

TABLE XI

Summary of Data for NaCl

$$1 = \text{Concentration} \times 10^3;\ 2 = \zeta;\ 3 = \frac{H\kappa_s}{P} \times 10^5;\ 4 = (\kappa_s - \kappa) \times 10^6$$

$$5 = \eta \times 10^2;\ 6 = \frac{\eta}{\kappa_s - \kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7;\ 7 = (\kappa_s - \kappa)\frac{P}{H\kappa_s} \times 10^{12}$$

1	2 mv.	3	4 mhos	5 poise	6	7
0.00	−10.00	− 9.90	20.5	0.950	45.44	−20.71
0.05	−12.83	−12.60	27.7	0.960	55.02	−21.99
0.10	−14.10	−14.10	32.2	0.938	57.99	−22.83
0.20	−13.75	−13.75	35.5	0.938	50.01	−25.81
0.40	−13.14	−13.30	41.7	0.925	39.27	−31.36
0.80	−12.07	−11.95	55.3	0.950	24.55	−46.29
1.60	−10.90	−10.90	67.0	0 938	16.61	−61.44

TABLE XII

Summary of Data for $MgCl_2$

$$1 = \text{Concentration} \times 10^3;\ 2 = \zeta;\ 3 = \frac{H\kappa_s}{P} \times 10^5;\ 4 = (\kappa_s - \kappa) \times 10^6;$$

$$5 = \eta \times 10^2;\ 6 = \frac{\eta}{\kappa_s - \kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7;\ 7 = (\kappa_s - \kappa)\frac{P}{H\kappa_s} \times 10^{12}$$

1	2 mv	3	4 mhos	5 poise	6	7
0.0	−14.36	−15.48	24.0	0.855	85.23	−15.5
0.1	−10.00	−11.05	30.2	0.83	33.5	−27.2
0.2	− 8.43	− 9.32	31.2	0.83	23.1	−33.4
0.4	− 8.02	− 8.50	35.9	0.874	20.2	−42.2
0.8	− 6.37	− 6.75	52.5	0.874	7.56	−77.7
1.6	− 2.39	− 2.69	40.0	0.84	15.20	−148.7

TABLE XIII

Summary of Data for $CaCl_2$

$$1 = \text{Concentration} \times 10^3;\ 2 = \zeta;\ 3 = \frac{H\kappa_s}{P} \times 10^5;\ (\kappa_s - \kappa) \times 10^6;$$

$$5 = \eta \times 10^2;\ 6 = \frac{\eta}{\kappa_s - \kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7;\ 7 = (\kappa_s - \kappa)\frac{P}{H\kappa_s} \times 10^{12}$$

1	2 mv	3	4 mhos	5 poise	6	7
0.0	−12.93	−13.70	27.8	0.874	58.89	−20.26
0.1	−10.10	−10.70	33.9	0.874	29.52	−31.66
0.2	−9.36	−9.55	36.2	0.916	23.06	−37.90
0.4	−9.36	−9.55	44.5	0.916	18.79	−46.59
0.8	−8.72	−8.90	51.0	0.916	14.22	−57.27
1.6	−8.69	−8.87	61.0	0.916	11.82	−68.75

TABLE XIV

Summary of Data for K_2CO_3

$$1 = \text{Concentration} \times 10^3;\ 2 = \zeta;\ 3 = \frac{H\kappa_s}{P} \times 10^5;\ 4 = (\kappa_s - \kappa) \times 10^6;$$

$$5 = \eta \times 10^2;\ 6 = \frac{\eta}{\kappa_s - \kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7;\ (\kappa_s - \kappa)\frac{P}{H\kappa_s} \times 10^{12}$$

1	2 mv	3	4 mhos	5 poise	6	7
0.0	−11.57	−11.50	14.23	0.945	87.86	−12.36
0.1	−16.44	−17.09	32.43	0.894	80.42	−18.97
0.2	−17.58	−17.40	66.50	0.950	43.14	−38.24
0.4	−17.19	−16.95	91.10	0.955	30.18	−53.75
0.8	−15.87	−15.78	133.6	0.945	17.65	−84.57

TABLE XV

Summary of Data for K_2SO_4

$$1 = \text{Concentration} \times 10^3;\ 2 = \zeta;\ 3 = \frac{H\kappa_s}{P} \times 10^5;\ 4 = (\kappa_s - \kappa) \times 10^{12};$$

$$5 = \eta \times 10^2;\ 6 = \frac{\eta}{\kappa_s - \kappa}\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7;\ 7 = (\kappa_s - \kappa)\frac{P}{H\kappa_s} \times 10^2;$$

1	2 mv	3	4 mhos	5 poise	6	7
0.0	− 9.63	− 9.58	16.63	0.945	52.12	−17.35
0.1	−12.16	−12.64	26.45	0.894	53.99	−20.92
0.2	−12.80	−12.62	38.73	0.955	39.24	−30.67
0.4	−11.39	−11.23	56.43	0.955	21.32	−50.22
0.8	−11.10	−11.04	90.4	0.945	12.78	−81.90

TABLE XVI

Summary of Data of K_3PO_4

$$1 = \text{Concentration} \times 10^3;\ 2 = \zeta;\ 3 = \frac{H\kappa_s}{P} \times 10^5;\ 4 = (\kappa_s - \kappa) \times 10^6;$$

$$5 = \eta \times 10^2;\ 6 = \frac{\eta}{\kappa_s - \kappa}\cdot\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7;\ 7 = (\kappa_s - \kappa)\frac{P}{H\kappa_s} \times 10^{12}$$

1	2	3	4	5	6	7
	mv		mhos	poise		
0.0	− 9.06	− 9.01	25.10	0.945	30.53	−27.83
0.1	−12.20	−12.69	38.38	0.894	37.58	−30.24
0.2	−16.41	−16.18	71.30	0.955	35.00	−44.06
0.4	−16.87	−16.89	95.72	0.937	27.79	−56.67
0.8	−13.61	−13.36	113.4	0.960	15.08	−84.94

TABLE XVII

Summary of Data for $ThCl_4$

$$1 = \text{Concentration} \times 10^3;\ 2 = \zeta;\ 3 = \frac{H\kappa_s}{P} \times 10^5;\ 4 = (\kappa_s - \kappa) \times 10^6;$$

$$5 = \eta \times 10^2;\ 6 = \frac{\eta}{\kappa_s - \kappa}\cdot\left(\frac{H\kappa_s}{P}\right)^2 \times 10^7;\ 7 = (\kappa_s - \kappa)\ \frac{P}{H\kappa_s} \times 10^{12}$$

1	2	3	4	5	6	7
	mv		mhos	poise		
0.00	− 9.92	−10.97	17.3	0.83	57.73	−15.76
0.05	− 7.44	− 8.23	14.23	0.83	39.52	−17.29
0.10	− 2.96	− 3.27	8.70	0.83	10.19	−26.60
0.20	+ 8.27	+ 9.14	1.51	0.83	45.92	+16.52
0.40	+11.96	+13.22	1.77	0.83	81.94	+13.38
0.80	+13.05	+14.43	14.81	0.83	116.7	+10.26
1.60	+13.14	+14.53	19.60	0.83	89.37	+13.48

Discussion

The curves in Figs. 2 through 9 present a clear and definite picture of what is happening at a water-cellulose interface as we increase the salt concentration of the electrolyte. In all cases, the charge on the double layer which is proportional to $(\kappa_s - \kappa\ P/H\kappa_s$ increases. This finding is not in agreement with the common idea which supposes an electrolyte to discharge the electrostatic charge on a surface. In general the thickness of the double layer which is proportional to $\left(\frac{H\kappa_s}{P}\right)^2 \frac{\eta}{\kappa_s - \kappa}$ decreases. That the thickness of the double layer decreases with increasing salt concentration has been demonstrated experimentally in the case of KCl solution in contact with gold electrodes by McClendon[8] and predicted from theoretical considerations by Gouy[9].

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[8] Science, 66, 200 (1927).

[9] J. Phys., (4) 9, 457 (1910).

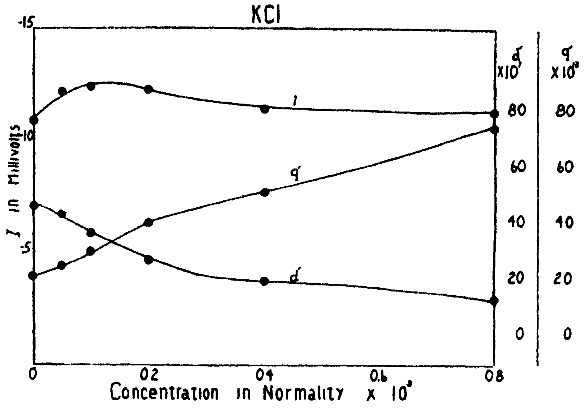

FIG. 2

Showing the effect of KCl on the electrokinetic conditions at a water-cellulose interface.

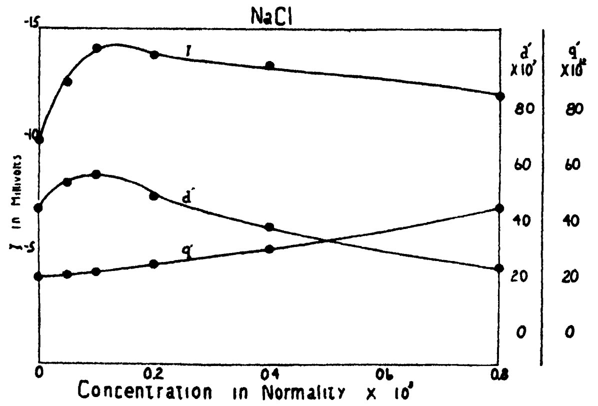

FIG. 3

Showing the effect of NaCl on the electrokinetic condition at a water-cellulose interface.

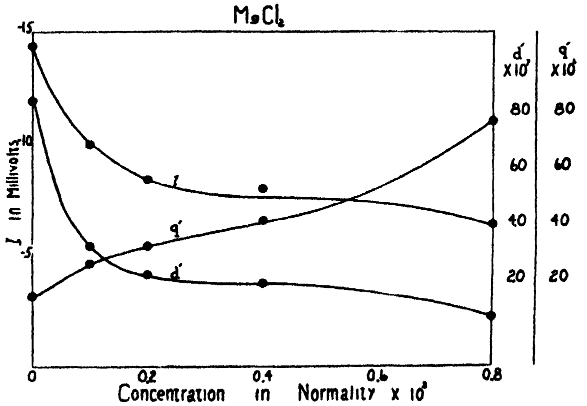

FIG. 4

Showing the effect of $MgCl_2$ on the electrokinetic conditions at a water-cellulose interface.

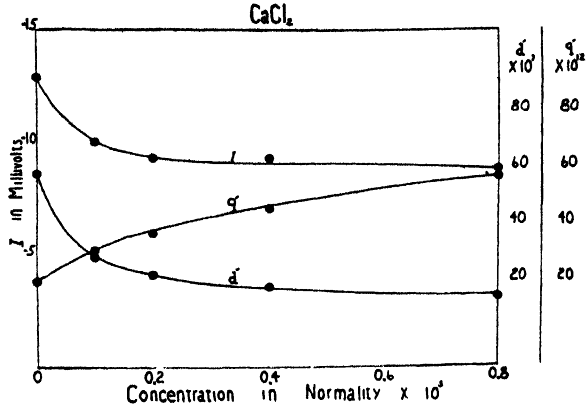

FIG. 5

Showing the effect of $CaCl_2$ on the electrokinetic condition at a water-cellulose interface.

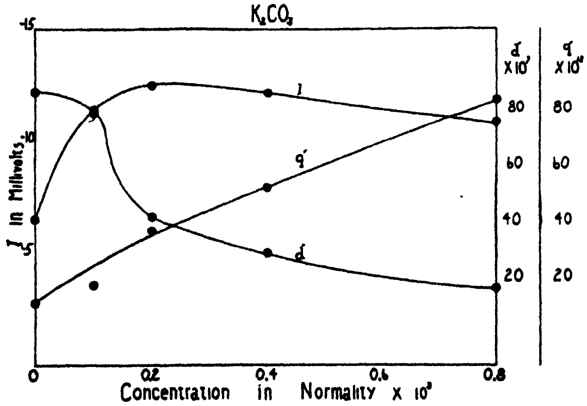

FIG. 6

Showing the effect of K_2CO_3 on the electrokinetic conditions at a water-cellulose interface.

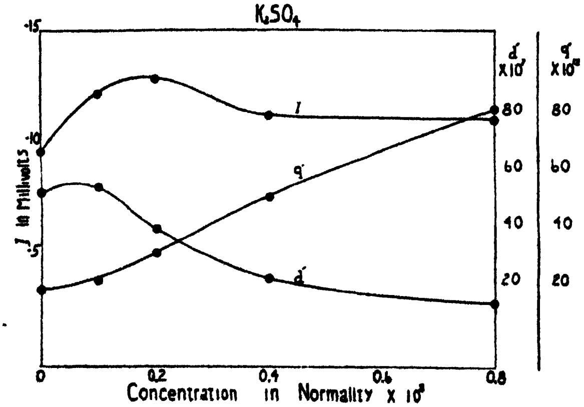

FIG. 7

Showing the effect of K_2SO_4 on the electrokinetic conditions at a water-cellulose interface.

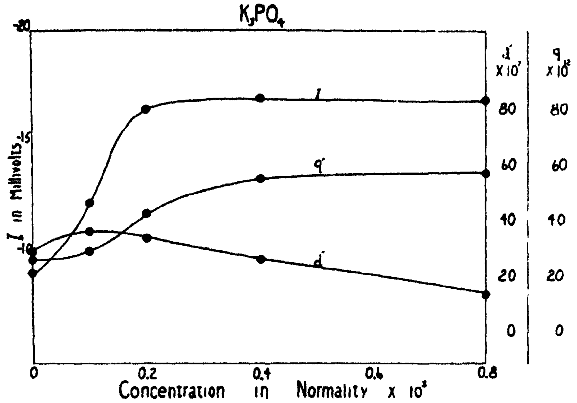

Fig. 8

Showing the effect of K_3PO_4 on the electrokinetic conditions at a water-cellulose interface.

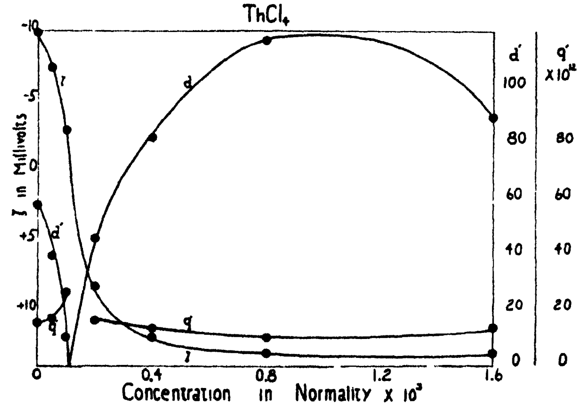

Fig. 9

Showing the effect of $ThCl_4$ on the electrokinetic conditions at a water-cellulose interface.

The curves for NaCl, K_2SO_4, and K_3PO_4 present some complications. The thickness of the double layer apparently at first suffers a slight increase followed by the usual decrease. We cannot at present say why this should be. It is, however, in sharp contrast to the usual view that the slight increase in the ζ-potential which is shown in these curves be due to an adsorption of anions, since this would have been evident in the curves showing the behavior of the charge with increasing salt concentration.

$ThCl_4$ is the only salt investigated which reversed the sign of the electric charge on the cellulose. It is very difficult to see exactly what is happening in this case, and to attempt an explanation at this time would be premature.

Perhaps the most important feature of this investigation is its bearing on our ideas of precipitation of colloidal particles by electrolytes. By definition the electrical work done in bringing two charged particles together is exactly equal to the ζ-potential, and it might be thought that the value of the ζ-potential would determine rather definitely the behavior of colloidal particles in the presence of electrolytes in respect to their effect on coagulation. This point has been brought out by Powis[10] who proposed a so-called critical potential to which the ζ-potential must be reduced before the colloidal particle can precipitate. We, however, while recognizing the importance of the electrical work term as expressed by the ζ-potential, feel that there are additional factors which must be considered.

It is not our purpose to propose a theory of precipitation but simply to point out that in the case of those monovalent cations where the ζ-potential of a colloidal particle is usually considerably higher than the critical potential when precipitation occurs, the action is simply to decrease the thickness of the double layer as is shown in the figures, allowing the particles to approach more closely before electrical repulsion is experienced and thus allowing a greater chance for molecular attraction between the colloidal particles to play a rôle. For example, with KCl the ζ-potential over the range of concentration investigated is almost constant but the thickness of the double layer has been decreased over 300 percent.

Summary

1. Smoluchowski's equation for surface conductance has been modified by the appropriate substitutions so that two equations were obtained, one expressing the charge per unit area on the surface and the other having to do with the thickness of the double layer.

2. The ζ-potential and surface conductance at a cellulose interface have been measured for aqueous solutions of KCl, NaCl, $MgCl_2$, $CaCl_2$, K_2CO_3, K_2SO_4, K_3PO_4, and $ThCl_4$.

3. The physical significance of the results are discussed. These studies indicate that the ζ-potential in general *decreases* with increasing concentration of electrolytes in the aqueous phase, but that this decrease in the ζ-potential may be accompanied by an actual *increase* in the charge on the particle, the decrease in the ζ-potential being more nearly related to a decrease in the thickness of the double layer.

4. The theoretical considerations of Gouy and the experimental findings of McClendon for KCl are confirmed for a series of electrolytes, *i.e.*, the thickness of the double layer is decreased with increasing salt concentrations.

5. A new conception of the action of electrolytes on affecting the stability of a colloid is suggested, *i.e.*, that the salts do not reduce the electric charge on the particle to zero or even to a "critical threshold," but rather that there is a *decrease in the thickness of the double layer* which allows the particles to approach each other closely enough so that they adhere to each other. With polyvalent ions, the charge itself may actually be decreased so as to approach zero.

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[10] Z. physik. Chem., 89, 186 (1915).

ELECTROPHORESIS AND THE DIFFUSE IONIC LAYER

BY MELVIN MOONEY*

Introduction

In a previous publication[1] the author has reported some electrophoresis measurements according to which the electrophoretic mobility of an oil drop suspended in distilled water increases with the diameter of the drop. A few measurements with dilute solutions of electrolytes indicated that electrolytes decrease this variation in mobility with diameter.

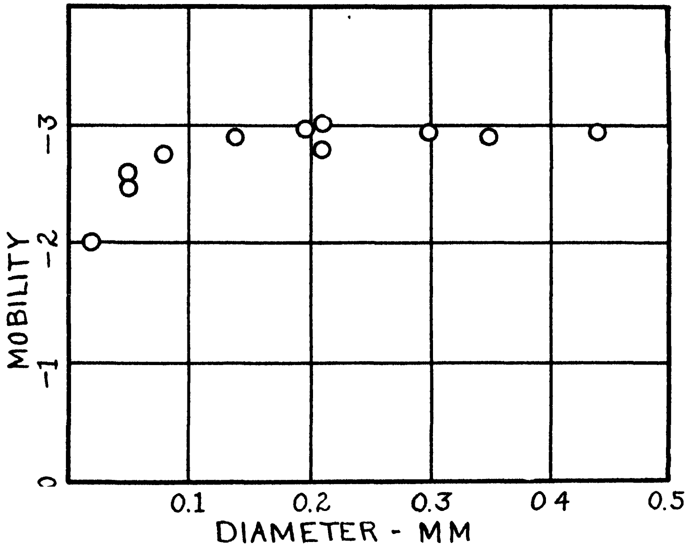

Fig. 1

Cataphoretic mobility of Red Oil and benzyl chloride measured in distilled water.

The nature of the mobility-diameter curve in distilled water is shown in Fig. 1. Alty[2] has reported that the mobility curve[3] of air bubbles in distilled water passes through a maximum at a diameter of about 0.2 mm; and he suggested that, if the author's measurements had been extended to larger diameters, there would have been found a maximum in the mobility curve for oil-drops also. The measurements plotted in Fig. 1 extend to diameters of nearly 0.5 mm; but they indicate only an asymptotic approach of the mobility to an upper limit.

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* Formerly National Research Fellow in Physics.

[1] Mooney: Phys. Rev., **23**, 396 (1924).

[2] Proc. Roy. Soc., **112A**, 235 (1926).

[3] The theory that will be outlined in the present paper cannot be tested with these data of Alty's, for two reasons; first, because his gas bubbles were not in equilibrium but were dissolving and decreasing continuously in diameter, and second, because all of his observed velocities require a correction for the electro-osmotic mobility, which was not determined.

Since the publication of the article just referred to, the effects of electrolytes on the mobility-diameter curve have been investigated in more detail; and a theory purporting to explain the experimental results has been developed. It is the purpose of the present paper to give a brief outline of the theory and to compare it with some of the experimental data. More details of the theory and the experiments will be given in a series of papers to be published elsewhere.

Current Theory

Up to the present time there have been published two theoretical formulas for electrophoretic mobility: the Helmholtz formula,[4] later modified by Lamb[5] and by Smoluchowski;[6] and the Debye-Hückel formula.[7] Since neither formula suggests or explains any variation in mobility with particle size, let us consider the necessary assumptions underlying these formulas. They are:

A—HELMHOLTZ	B—DEBYE-HÜCKEL
1. The particle is rigid and non-conducting.	1. The particle is rigid and spherical.
2. D, the dielectric constant and η, the coefficient of viscosity, have the same values within the electric double-layer as in the liquid in bulk.	2. Identical with A2.
3. The charge distribution in the double-layer is unaffected by the impressed field or by the relative motion of the particle and the suspension medium.	3. The spherical symmetry of the charge distribution in the double-layer is unaffected by the impressed field or by the relative motion of the particle and the suspension medium.
4. The thickness of the double-layer is small in comparison with the radii of curvature of the particle surface.	4. The thickness of the double-layer is large in comparison with the radius of the particle.

The formulas obtained on these assumptions are:

$$\mu_e = \frac{v}{E} = \frac{D\varphi}{4\pi\eta} \quad (1)A \qquad\qquad \mu_e = \frac{v}{E} = \frac{D\varphi}{6\pi\eta} \quad (1)B$$

in which μ_e is the electrophoretic mobility, v the velocity, E the impressed field, D the dielectric constant, η the coefficient of viscosity of the liquid, and φ the potential at the surface. The difference between the assumption A4 and B4 accounts for the difference between the two resulting formulas.

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[4] Helmholtz: Ann. Physik, 7, 337 (1879); Mem. London Phys. Soc. (1888); Ges. Abhandl. Kenntnis Kohle, 1, 855 (1922).

[5] Lamb: Brit. Ass. Adv. Sci. Repts., 495 (1887); Phil. Mag., 25, 52 (1888).

[6] Smoluchowski: Bull. intern. acad. sci. Cracovie, 182 (1903).

[7] Debye and Hückel: Physik. Z., 25, 49, 204 (1924).

The assumption B4 is not mentioned in the Debye-Hückel articles; and indeed no one seems to realize that such an assumption is involved. In fact, however, this condition is necessary to the validity of the Debye-Hückel analysis, the reason being that those authors neglected the electric polarization of the particle under the influence of the impressed field. In doing so they necessarily neglected also the interaction between the polarization charges and the mobile charge of the double-layer; and this interaction would produce an appreciable effect on the mobility if an appreciable fraction of the mobile charge were situated close to the particle.

Assumption A2, or B2, concerning the constancy of D and η, has been subjected to criticism,[8] and it is certainly reasonable to expect some change in the values of these "constants" due to the special forces within one or a few molecular diameters from a surface. However, if we consider the tendency of the mobile ions to diffuse away from the surface, we arrive at a picture, first drawn for us by Gouy,[9] in which the thickness of the double layer often far trancends the limits of these surface forces. Furthermore, present day knowledge concerning the nature of adsorbed layers leads us to reject as very improbable any surface slip such as was considered by both Helmholtz and Lamb.

Theory of Electrophoresis based on the Diffuse Layer

In the author's attempts to improve the theory of electrophoresis, assumption A2 has been retained and assumptions A3 and A4, B3 and B4 have been rejected as being much less acceptable. The rejected assumptions are replaced with a quantitative theory of the charge distribution in the outer, mobile part of the double-layer, hereafter termed the ionic atmosphere or the diffuse layer. Specifically, it is assumed:

a. The particle is spherical, non-conducting, or surrounded by a non-conducting surface, and is rigid—at least to the stresses involved in electrophoresis. The liquid in which the particle is suspended contains in solution a single di-ionic electrolyte.

b. The ions in the diffuse layer move in accordance with established physical laws, under the influence of 1, the velocity of the water; 2, the local electric field; 3, diffusion.

c. D, η, and also m_1 and m_2, the absolute mobilities of the positive and negative ions, respectively, are constant up to the spherical surface enclosing the particle and any rigidly adsorbed material.

As in previous analyses of electrophoresis, the inertia terms in the hydrodynamic equations are neglected in comparison with the viscosity terms. The formulas obtained are consequently valid only for small velocities.

It is obvious that, on the basis of assumption *b*, the mean thickness of the Helmholtz double-layer will vary with the concentration and valence of the electrolytic ions, the conditions reducing to Gouy's theory in the special simple case of an infinite sphere (plane surface) with zero impressed field. The mobility of a finite spherical particle will be shown to depend theoretically upon the ratio of its radius to the mean thickness of the diffuse layer.

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[8] Harkins: Colloid Symposium Monograph, **6**, 17 (1928).

[9] Compt. rend., **149**, 654 (1909); J. Phys., **9**, 457 (1910).

The system of differential equations representing my assumptions is too complicated to allow any hope for a complete solution; but I have succeeded in obtaining the first two terms of the solution in the form of a power series in χ, the surface curvature:

$$\mu_e = -\left\{\frac{D\varphi}{4\pi\eta} + \chi F_1(\varphi) + \sum_2^\infty{}^i \sum_2^\infty{}^j F_{ij}(\varphi)\chi^i E^j\right\} \tag{2}$$

in which χ is the surface curvature, or $1/r$, r being the radius of the sphere; F_1 is a known function of φ, and the F_{ij}'s are undetermined functions of φ. The first term in this formula is the familiar Helmholtz mobility formula. The second term gives the first order correction for the curvature of a finite sphere. The remaining terms all involve higher powers of χ and E.

For purposes of comparison with experiment it is convenient to differentiate equation (2) with respect to χ, thus obtaining an expression for S_0 the limiting slope at zero curvature,

$$S_0 = \left(\frac{\partial\mu_e}{\partial\chi}\right)_0 = -\frac{2t\mu_0}{\varphi}\left(\lambda_1 + \frac{2DA}{\pi\eta}\lambda_2 + \lambda_3\right) \tag{3}$$

in which

$$\lambda_1 = 6\int_0^\omega \ln\frac{1+x}{1-x}\cdot\frac{dx}{x} - \frac{8\omega}{3(1+\omega)}\ln(1+\omega) - \frac{8\omega}{3(1-\omega)}\ln(1-\omega)$$

$$\lambda_2 = \frac{1}{m_1}\ln(1+\omega)\left[\ln\frac{1+\omega}{1-\omega} - \frac{2\omega}{1+\omega}\right] + \frac{1}{m_2}\ln(1-\omega)\left[\ln\frac{1+\omega}{1-\omega} - \frac{2\omega}{1-\omega}\right]$$

$$\lambda_3 = 4\omega\frac{1-\omega^2}{1+\omega^2}$$

$$\omega = \sinh\frac{\varphi}{2A} \qquad A = \frac{kT}{\nu e}$$

$$t = \sqrt{\frac{DkT}{8\pi n e\nu^{22}}}$$

μ_0 is the limiting (extrapolated) mobility at zero curvature, k is the Boltzmann constant, T the absolute temperature, n the number of ions of one kind per ml of solution, ν the valence of the ions, and e is the electronic charge. The definitions of the other terms are the same as have already been given.

The term λ_3 does not occur in these equations if it is assumed that the surface potential, φ, is independent of χ; but it does occur if it is assumed that it is σ, the surface charge, that is independent of χ. It can be argued on very reasonable grounds that these assumptions represent the two extreme possibilities and that the actual situation lies somewhere between the two. Fortunately, λ_3 is found to be small in comparison with the other terms in equation (3); and in view of the present inaccuracy in electrophoresis measurements, we do not need to concern ourselves further with the exact variation of φ or σ with χ.

In testing equation (3) with experimental data, the value of φ is calculated from μ_0 by means of the Helmholtz formula. ω and the λ's are thereby determined; and the right member of equation (3) is evaluated by inserting the proper values of the parameters.

Experimental Procedure

The electrophoretic mobilities of oil drops suspended in various solutions of electrolytes were determined, the microscopic method being used. The electrophoresis cells employed were thin-walled, cylindrical glass U-tubes immersed in a small water bath. The oil phase in the suspensions was always quite small, 1 per cent or less. The suspensions were formed in some cases by shaking a few drops of oil with 100 or 200 ml of water or aqueous solution in a separatory funnel; in other cases by squirting into the water or solution a fine stream of oil under high pressure. The following oils were used, either singly or combined in mixtures of the same density as the solution used:—phenyl chloride, phenyl bromide, anisol, anethol, Stanolind and Red Oil, the last two being commercial paraffin hydrocarbon oils manufactured by the Standard Oil Company.

Measurements at room temperature were made without any thermostatic control. The data thus obtained were recalculated to the standard basis of 20°C on the assumption that all mobilities would merely be changed inversely as the viscosities of the water at the two temperatures considered.

The precision attained in this work was better than that in most measurements of electrophoresis, the mean error being 1 per cent or less under favorable conditions. Nevertheless, this precision is obviously not at all what it should be for testing a theory which predicts only the limiting slope of the mobility curve at zero curvature; that is, at infinite radius.

A still greater hindrance to accuracy in determining the limiting slope was found to lie in the suspensions themselves. They were difficult to reproduce; and in the more concentrated electrolyte solutions they seldom gave smooth mobility curves. Generally many drops of the same diameter were found with widely different mobilities. Consequently, all that can be done with the experimental data is to determine very roughly the limiting slope of the mobility curve and see whether or not the theoretically predicted slope is correct in its order of magnitude.

Comparison of Experimental Results with Theory

In Fig. 2 are shown some electrophoretic mobilities, plotted against curvature, in various concentrations of KOH. Extrapolation to zero curvature gives us μ_0, from which we calculate the limiting slope of the mobility curve as χ approaches 0. These theoretical slopes and the values assumed for μ_0 are indicated by the straight lines in the figure. It is seen that the theoretical

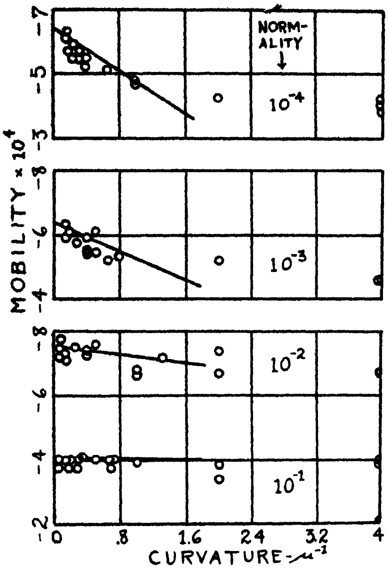

Fig. 2

Cataphoretic mobilities in cm/sec/volt/cm, measured in KOH.

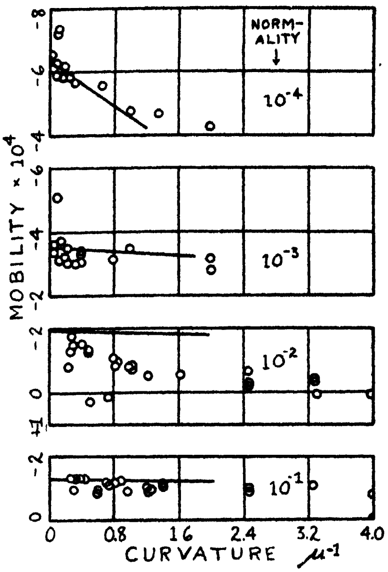

Fig. 3

Cataphoretic mobilities in cm/sec/volt/cm, measured in KCl.

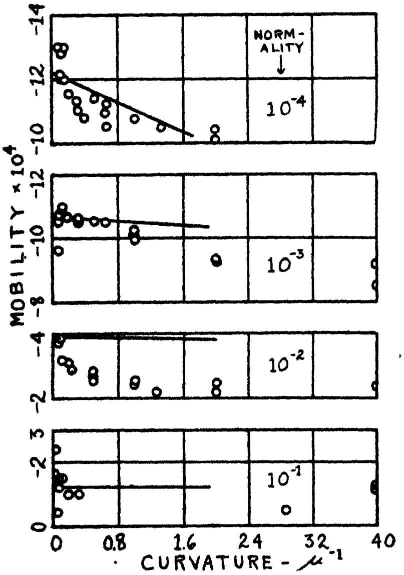

Fig. 4

Cataphoretic mobilities in cm/sec/volt/cm, measured in KCl.

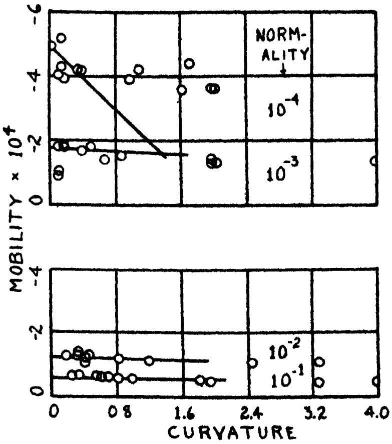

Fig. 5

Cataphoretic mobilities in cm/sec/volt/cm, measured in $CuSO_4$.

slope rapidly approaches zero as the concentration increases and is in rough agreement at all concentrations with the experimental slope.

Figure 3 shows a series of measurements made in KCl solutions. The agreement between theory and experiment is satisfactory with concentrations up to 10^{-3} molar; but at the higher concentrations definite disagreement appears. The difference between the theoretical and experimental slopes in 10^{-1} molar KCl is not large; but their ratio appears to differ considerably from unity. In the next series, Fig. 4, with HCl as the electrolyte, the agreement between theory and experiment is still good with the dilute solutions; but with the concentrated solutions the disagreement is more pronounced than with concentrated KCl. In Fig. 5 are shown the results obtained with $CuSO_4$, a salt with bivalent ions; and the agreement here seems to be good throughout the entire series. The calculations in this case are based on the assumption that the $CuSO_4$ is partially ionized but not hydrolyzed at all. Fig. 6 shows some cataphoretic mobilities at 75°C. The theory agrees with the experimental results except in the case of 0.5×10^{-2} molar $CuSO_4$.

To summarize these results, it can be said that the theoretical slope of the mobility-curvature curve agrees fairly well with the experimental data for dilute solutions up to concentrations of 10^{-3} molar and in some cases for the more concentrated solutions. Assuming that such agreement as is obtained is not accidental, but results from the essential soundness of the theory, we have yet to explain the lack of agreement for concentrated neutral and acid solution.

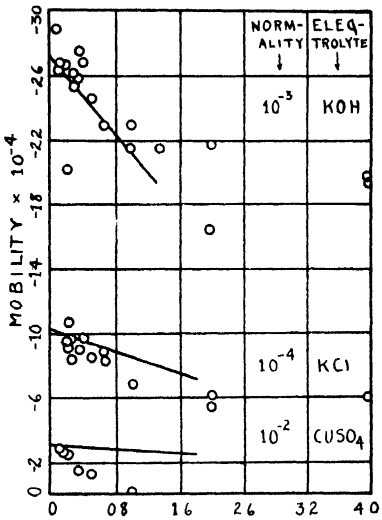

FIG. 6

Cataphoretic mobilities in cm/sec/volt/cm, measured at 75°C.

Early in this program of research the question was examined as to how soon equilibrium is established between the surface charge and the ionic atmosphere surrounding the drop. Suspensions of oil in distilled water, in 10^{-3} molar KOH and HCl and in weaker solutions of KOH, were examined when formed and also after ageing for several days; but no significant changes in electrophoretic mobilities were found. Extended ageing experiments with more concentrated solutions were attempted but failed, because of the instability of the oil suspensions. On the basis of the results in dilute solutions, it was assumed that in all cases an oil-water interface attains its equilibrium surface charge practically as soon as it is formed.

However, certain other experimental results in addition to those already shown led to a re-examination of the question of equilibrium. Greater stability of the suspensions was attained by using mixtures of oils having practically the same densities as the electrolytic solutions in which the oils were suspended. Fig. 7 shows some data obtained with 10^{-2} molar HCl. The "hot" suspensions were made by atomizing the oil in boiling hot solution. The suspension was then allowed to cool slowly—in an hour or two—to room temperature before filling the electrophoresis cell. It is obvious that the cold suspension on the second day had changed from what it was when fresh, but had not yet reached the state of the "hot" suspension, which appears to be more stable. A series of such experiments indicated that, in all cases in which the theoretical slope of the mobility-curvature curve departed notably from the experimental curve, the suspension was not in its equilibrium state.

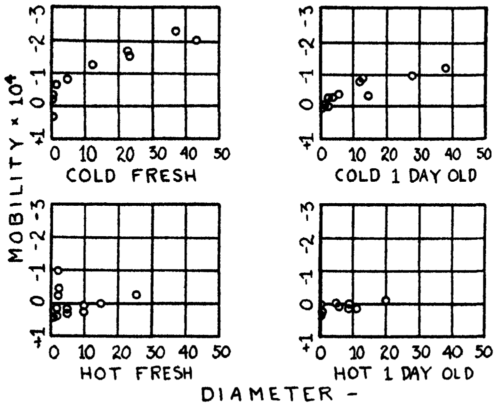

FIG. 7

Cataphoretic mobilities in cm/sec/volt/cm, measured in 10^{-2} molar HCl. "Hot" indicates a suspension formed in boiling hot solution and cooled slowly to room temperature. "Cold" indicates a suspension formed at room temperature.

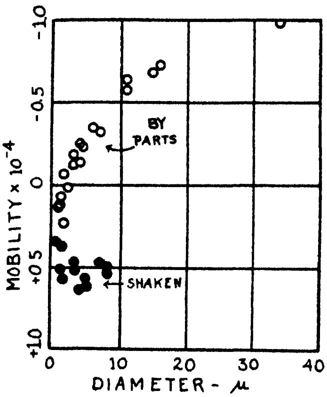

FIG. 8

Cataphoretic mobilities in cm/sec/volt/cm, measured in 10^{-1} molar HCl. "Shaken" indicates suspension formed by shaking oil with the acid solution. "By parts" indicates suspension formed by shaking oil with water and then adding the acid.

Logically the next step in the experimental procedure would be to produce suspensions that are in equilibrium; but this seems to be very difficult to do, at least if we assume as one criterion of equilibrium that all drops of the same diameter must have the same electrophoretic mobility. Since the oil drops coalesce, extended ageing cannot be used; and no method of preparing the fresh suspensions was found which gave reproducible, smooth and stable mobility curves. This difficulty is much greater with acid than with neutral or alkaline solutions. It is illustrated in Fig. 8, which shows the different results obtained, when the suspension is formed by shaking the oil in a 10^{-2} molar solution of HCl, in the usual manner, and when it is formed "by parts", by shaking the oil in distilled water and adding the acid afterwards. The latter method is the only one that gives a definite curve, but ageing and other tests show that the suspension thus formed is further removed from equilibrium than the one formed by the first method.

Anomalous Effects

Considerable effort was spent in trying to determine the disturbing factor that was interfering with the establishment of equilibrium. In addition to the effect just mentioned, depending upon the method of preparing the suspension, a variety of other anomalous effects were thus discovered. Either ageing or temporary heating may sometimes increase and sometimes decrease the mobility. There are both permanent and temporary changes in mobility with the duration of the impressed field; and the mobility sometimes varies with the intensity of the impressed field. By coating the wall of the electrophoresis cell with the oil used in the suspension, the ratio of electrophoretic mobility of the large drops to the electro-osmotic mobility was determined. This ratio was found to vary considerably. For suspensions which were normal in other respects, it was 1, which is the theoretical ratio on the basis of the Helmholtz theory. For suspensions which were abnormal in other respects, the ratio was usually greater than 1, the largest observed ratio being 2.

All these and several other anomalous effects taken together can scarcely be said to establish the underlying cause of the anomalies. Nevertheless, they all seem to indicate or allow an explanation based on the following "slow motion" picture of the formation of the Helmholtz double-layer:

1. As soon as an oil-water surface is formed, adsorption of ions from the water begins. In general, ions of opposite sign will not be adsorbed equally; and a net surface charge will result.

2. The surface charge attracts ions of the opposite sign and repels ions of the same sign and thereby causes the development of a diffuse ionic layer in the water near the surface.

3. The surface forces, including that due to the surface charge, generally cause strong adsorption of water and electrolyte molecules. These adsorbed molecules sometimes form a semi-rigid crust or plastic layer between the surface and the diffuse layer. The plastic layer may be many molecules deep and its growth may occupy seconds, minutes or even hours; but as soon as it begins to form, it interferes with the further adsorption of ions by the surface and hence tends to stabilize the surface charge before true equilibrium has been reached.

In order to make this picture consistent with experimental results, it is necessary further to postulate that the plastic layer has a volume charge of the same sign as that of the diffuse layer, that it can be more or less disrupted by mechanical or electric forces, and that in electrokinetic processes it is more easily dislodged from a finite sphere than from a plane surface.

The first two elements of this picture, the adsorbed surface charge and the diffuse ionic layer, have already been depicted in many of the recent discussions of electro-kinetic phenomena. The third element, also, the layer of adsorbed molecules, enters into some of these discussions;[10,11] and its existence is further indicated by a large number of phenomena other than electro-

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[10] Gyemant: Z. Physik, **17**, 190 (1924); "Kolloidphysik," (1925).

[11] Stern: Z. Elektrochemie, **30**, 508 (1924).

kinetic, such as the hydration of colloids, precipitation under conditions that permit peptization, thixotropy, plastic oil-water surfaces which the author has observed in the presence of $FeCl_3$, and the lack of adhesion[12] in some cases between the particles of a suspension and a glass surface. There is thus plenty of precedent for postulating this third element in the picture of the double-layer. The novel features suggested here are the susceptibility of this molecular or poly-molecular layer to external forces and its interference with ionic diffusion and interchange between the surface and the diffuse ionic layer.

Surface Charge

Preliminary to analyzing the diffuse ionic layer around a sphere, it was necessary, among other things, to find the relationship between the electrokinetic potential and the surface charge of a plane surface. This relationship is

$$\sigma = \frac{\mathrm{LA}}{\pi l} \cdot \frac{\omega}{1 - \omega^2} \tag{4}$$

In Fig. 9 are plotted on a logarithmic scale values of σ calculated from μ_0, the limiting electrophoretic mobilities of oil drops.

Surface Conductivity

As a consequence of the tangential motion of the mobile ions in the double-layer, there will be an increment in the conductivity of the liquid near a surface. The value of this increment per unit area of a plane surface, or the specific surface conductivity, κ, will be expressed by an integral of the form

$$\kappa = \int_0^\infty \Big[(\rho_1 - \rho\ )\,(\mathrm{m}_1 + w) + (\rho_2 - \rho_\infty)\,(\mathrm{m}_2 - w) \Big] \mathrm{dx} \tag{5}$$

or

$$\kappa = \int_0^\infty \Big[(\rho_1 - \rho_2)w + (\rho_1 - \rho_\infty)\mathrm{m}_1 + (\rho_2 - \rho_\infty)\mathrm{m}_2 \Big] \mathrm{dx} \tag{6}$$

in which ρ_1 and $-\rho_2$ are the charge densities due to the positive and negative ions, respectively; ρ_∞ is the charge density outside the diffuse layer due to the positive ions; w is the velocity of the water under unit field; m_1 and m_2 are the absolute mobilities of the positive and negative ions, respectively; and x is the distance from the surface. The term, $(\rho_1 - \rho_2)w$, expressing the current due to the net charge carried by the water, is the only term included in Smoluchowski's formula for surface conductivity.[13] The other two terms in the integrand of equation (6) represent the current due to the motion of the ions with respect to the water.

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[12] Buzágh: Kolloid-Z., **51**, 105 (1930).

[13] Smoluchowski: Physik. Z., **6**, 529 (1905).

The indicated integration can be accomplished without difficulty in the case of a di-ionic electrolyte, yielding

$$\kappa = \sigma\mu_e\left(1 - \frac{2\omega A}{\varphi}\right) + \sqrt{\frac{2DkTn}{\nu}}\left(-\frac{m_1\omega}{1+\omega} + \frac{m_2\omega}{1-\omega}\right) \tag{7}$$

in which μ_e is now the electro-osmotic mobility. The rest of the notation is the same as in previous sections. We can test this formula with the measurements of absolute conductivity of plane surfaces recently reported by McBain and Peaker.[14] They found $\kappa = 4.3 \times 10^{-8}$ mhos for polished glass in contact with 10^{-3} molar KCl at 25°C, and $\kappa = 3.5 \times 10^{-8}$ mhos for a stearic acid film on distilled water. For the electro-kinetic potential of glass against the salt solution we can use the figure 0.8 millivolt, reported by Powis.[15] Equation (7) then gives us $\kappa = 8.5 \times 10^{-10}$ mhos, which is only 0.02 of the experimental value. No figure is available for the electro-kinetic potential of stearic acid in water; but from the order of magnitude of all such potentials we know that in this case also equation (7) will give a value for κ many times too small. From these discrepancies we must conclude that there are other factors contributing to the surface conductivity in addition to what we have considered. What they may be can only be surmised; but it is noteworthy in this connection that Bancelin[16] found that a glass surface adsorbs 14×10^{-8} g/cm² of NaCl from a 10^{-4} molar solution. If the surface was plane, this adsorption figure corresponds to 1.1 molecular layers with the molecules normal to the surface; that is, 1.1 double ionic layers. If we assume that these molecules are oriented, some with their chlorine atoms and some with their sodium atoms towards the glass, that some of them are completely ionized, and that many of them are partially ionized in such a way that the ion on the water side of the surface is free to move parallel to the surface, but not normal to it—then we have a picture which meets all the requirements of the theory of the diffuse layer and of the experimental measurements of surface conductivity and of electro-osmotic mobility.

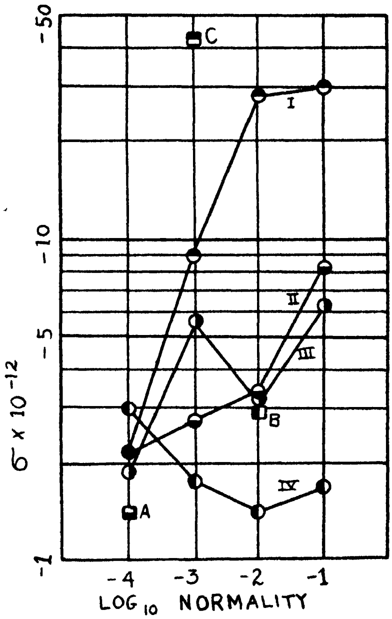

FIG. 9

Surface charge expressed as the number of elementary charges per cm².

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[14] Proc. Roy. Soc., **125A**, 394 (1929).

[15] Z. physik Chem., **89**, 91 (1915).

[16] J. Chim. phys., **22**, 518 (1925).

The conductivity of the stearic acid-water surface presents a different problem; for in this case we know that practically all of the acid molecules are turned the same way, with the $-COOH$ group towards the water. In order to explain the large surface conductivity in this case, it is necessary to assume either that impurities in the water are adsorbed and behave like the NaCl in the preceding picture or that the ionization of the water itself is increased in the neighborhood of the surface.

The plastic adsorbed layer, postulated in section 6, has not entered into this discussion of surface conductivity, because NaCl or KCl are not very active in forming a plastic layer. Among the electrolytes which were used in the author's work the most active in this respect were $FeCl_3$, $Zr(NO_3)_4$, and $Th(NO_3)_4$, all of which are salts with poly-valent cations. Recently Briggs[17] has measured the relative surface conductance of cellulose fibers (filter paper) in several electrolytic solutions; and he found that the surface conductance is increased by HCl and KCl, but very little affected by $ThCl_4$. We cannot avoid the suggestion here that the activity of $Th(NO_3)_4$ in building up a plastic adsorbed layer and the inactivity of $ThCl_4$ in promoting surface conductance are closely associated phenomena.

Discussion

The present state of the theory and general understanding of electro-kinetic phenomena is deplorably chaotic. Some writers are using the Debye-Hückel formula for calculating electro-kinetic potentials, while others stick to the Helmholtz formula. Those who are trying to determine experimentally which of the two formulas is "right" do not consider the difference in the derivations of the formulas or discuss adequately the significance of an experimental discrimination. Recently Thon[18] has questioned whether the electro-kinetic potentials as determined by electrophoresis and by streaming potential are essentially the same thing, as has always been assumed; and both Harkins[8] and McBain[19] have argued that the "electro-kinetic potential" does not exist or mean anything, anyhow. In this rather extended discussion an attempt will be made to clarify and settle some of these cloudy questions.

The original Helmholtz conception of a very thin electric double-layer of atomic dimensions is frequently criticized, usually on the basis of Gouy's theory of the diffuse ionic layer; and sometimes the conclusion is drawn that the Helmholtz analysis of electro-kinetic phenomena must be discarded. However, it has been shown in this paper that when we make a quantitative analysis of the effect of the diffuse layer, considering also its distortion during electrophoresis, we find that the first approximation to the electrophoretic mobility of a large sphere is the familiar Helmholtz formula. It can likewise be shown that the Helmholtz analysis is valid for any surface in water or aqueous solutions, so long as the radii of curvature are large in comparison with the thickness of the double-layer.

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[17] Colloid Symposium Monograph, **6**, 41 (1928).

[18] Z. physik. Chem., **147**, 147 (1930).

[19] J. Phys. Chem., **28**, 706 (1924).

Furthermore, barring mathematical blunders, there can be no question concerning the fundamental validity of the theory of the diffuse ionic layer as it has been outlined in this paper; for the theory is based upon well-established physical laws which have their origin and proof in lines of experiment entirely outside of electro-kinetic phenomena. The only assumption *ad hoc* is that the moving particle has an electric charge, and that is really a conclusion necessitated by the visible motion of the suspended particle. Consequently, even if the theory is found to disagree completely with the data obtained under any particular experimental conditions, we cannot conclude that the theory is false. We have only proved that it is incomplete or that incorrect values have been assigned to the parameters involved.

As for the incompleteness, a number of experimental results in electrophoresis have already been interpreted in this paper as being due to the strange behavior and interference of a plastic or semi-solid adsorbed crust which was not contemplated in the theory.

Concerning the values of the parameters close to a surface, we do not have entirely satisfactory information; but it is yet to be proved that the values there are much different from what they are in the liquid in bulk. Kallmann and Dorsch[20] have measured the dielectric constant of films of liquids about $1\mu_0$ thick; and they found no perceptible difference from the normal values. No variation in dielectric constant less than their mean error, about 0.2 per cent, could have any important effect on the charge distribution in a diffuse layer that extends several $m\mu$ from the surface.

Concerning the viscosity near a surface, if there is any deviation at all from the normal value, current theories of surface structure would lead us to expect an increase, associated with more or less molecular orientation. Any electro-kinetic phenomenon would tend to disturb this special orientation of the molecules, if it exists; and we would anticipate some lack of proportionality between cause and electrokinetic effect. For example, Ettisch and Zwanzig[21] found a variation in streaming electro-kinetic potential with pressure when forcing mixtures of methanol and water containing a trace of KCl through glass capillaries; and a variation in cataphoretic mobility with impressed field in some of my own measurements has already been mentioned. But in the absence of such abnormal effects there is no reason for doubting that in dilute and moderately concentrated solutions, the viscosity is constant throughout the greater part of the double-layer. In view of these considerations the conclusion seems justified that, with limitations of the kind that have been discussed, the Helmholtz analysis of electro-kinetic phenomena is applicable whenever the curvature of the surface involved is small in the sense previously indicated.

Unfortunately, the situation is quite different in regard to surfaces of large curvature. The system of differential equations resulting from the author's set of assumptions can probably be solved for the mobility as a power series in φ, the electro-kinetic potential; and such a solution would be valid for a sphere of any size, provided that φ were sufficiently small. But the development of this solution still remains for the future.[22] The Debye-Hückel mobility formula can be used for a small sphere in a very dilute solution; but the assumptions B3 and B4 of section 2 are such severe restrictions that the applicability of the formula is limited to very dilute solutions and to ultramicroscopic micelles, composed of only a few molecules and carrying only a few elementary charges. In between the regions covered by the Helmholtz and the Debye-Hückel theories there is a large region in which the radii of surface curvature are of the same order of magnitude as the Gouy diffuse layer. This region is a "no-man's land," not yet belonging to either theory. Obviously, ignoring these limitations of the theories will lead to false deductions and to confusion. This fact is illustrated in Thon's suggestion that electrophoresis and electro-osmosis are different in some fundamental way not yet understood. The indiscriminate application of Stokes' law and the treatment of all colloids as electrolytes are violations of the restrictions upon the Debye-Hückel electrophoresis theory. Some of the discrepancies that result in this case have already been discussed by Pauli and Valkó.[23]

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[20] Z. physik. Chem., **126**, 305 (1927).

[21] Z. physik. Chem., **147**, 151 (1930).

Summary

1. The theory of the diffuse ionic layer and its influence on the electrophoresis of a sphere is outlined and a theoretical formula for the limiting slope of the mobility-curvature curve is given.

2. Experimental data are reported which are in rough agreement with the theory as applied to dilute aqueous solutions. In concentrated solutions there is definite disagreement in some cases.

3. Formulas are given for surface charge and surface conductivity. The latter formula does not agree with measured values.

4. Various anomalous effects in cataphoresis suggest the existence of a plastic adsorbed layer which seems to have a profound effect on the electrokinetic potential in concentrated acid and neutral solutions.

5. It is pointed out that the validity of the Debye-Hückel cataphoresis formula is limited to conditions in which the colloidal particle is much smaller than its diffuse ionic layer.

The experimental work reported in this paper was done at the Ryerson Physical Laboratory of the University of Chicago. I am greatly indebted to Professor A. C. Lunn and other members of the faculty for their assistance and interest. I feel quite incapable of expressing my gratitude to the University for the facilities placed at my disposal, especially as an appreciable part of the work was done during my spare time after I was no longer officially connected with the Laboratory, and at a time when space was very much in demand for full-time research workers. To the National Research Council, I am greatly indebted for their long-continued support in a baffling problem.

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[22] The corresponding analysis of electro-osmosis in a straight capillary tube of small radius has recently been published by Komagata: Bull. Chem. Soc. Japan, 4, 255 (1929).

[23] "Elektrochemie der Kolloide," 268 (1929).

POTENTIAL DIFFERENCES AT AIR-LIQUID INTERFACES

BY JOHN WARREN WILLIAMS AND V. A. VIGFUSSON

It is well known that the electrical phenomena with which we have to deal in colloidal chemistry are quite different from those which may be treated thermodynamically to form what we know as electrochemistry. Indeed, in colloidal chemistry it is necessary to consider just those electrical phenomena which are neglected in ordinary electrochemistry. The relationship between the electrokinetic potential and the thermodynamic potential has been the subject of much investigation, yet, in spite of this fact, there remains much to be learned about the electrokinetic potential.

There exists an electrokinetic potential at the various types of interface, solid-liquid, liquid-liquid, liquid-gas, etc. This potential, called the ζ-potential, is measured *tangentially* to the interface between the two phases. In other words, it is necessary to assume that a layer of the more mobile phase adheres to the surface of the less mobile phase in order to measure it. The most familiar methods for this purpose are electroendosmose and cataphoresis.

More recently there have been reported in the literature determinations of potential differences which have been measured *vertically* to the interface. Since in the case of both the tangential and vertical measurements adsorption exerts such a pronounced influence it might have been suspected that the two potential differences were at least quite intimately related to each other. As yet, however, the meagre experimental data indicate that such is not the case. It is not the purpose of the present article to make this comparison, rather, we shall limit the discussion to the potential differences which have been measured in a vertical direction across the liquid-air interface. These potentials are found to be absolutely dependent upon the composition of the surface layer of molecules limiting the liquid phase. This layer is definitely an adsorption layer whose composition may be determined more or less exactly by noting the changes in surface tension caused by dissolved substances in accordance with the well-known equation of Gibbs.

Because of these facts it appears that it should be possible to calculate from the magnitude of the observed potential difference the electric moment of any molecule which does not dissociate and which is adsorbed in the surface layer. This calculation necessarily involves the assumption that the molecules be imagined as arranged in a parallel layer perpendicular to the interface. The following relation may be shown to hold between the potential difference, E, and the electric moment of the molecule, μ.

$$E = 4\pi N\Gamma\mu,$$

$$\text{or}\,\mu = \frac{E}{4\pi N\Gamma}\,.$$

In this equation N is the Avogadro number and Γ is the surface concentration in gram mols per square centimeter. The quantity $4\pi N\Gamma$ may be found from surface tension measurements.

Using this equation Rideal[1] calculates the electric moment of the butyric acid molecule to be

$$\mu = 0.3 \times 10^{-18} \text{ e.s.u.}$$

In recent years the Debye modification of the Clausius-Mosotti relation has made it possible to determine the electric moment of a molecule either from the temperature coefficient of the dielectric constant of its vapor or from dielectric constant and density data for a binary liquid mixture composed of a non-polar solvent and the molecule in question as solute. The values of the electric moments of molecules determined in this way are now universally considered to be quantitatively correct, provided, of course, that complicating chemical influences are not operative in the vapors or solutions.

There has been reported recently a value for the moment of butyric acid by Wolf[2], $\mu = 0.7 \times 10^{-18}$ e.s.u., obtained from dielectric constant and density data for its benzene solutions. It is therefore evident that the value calculated from the observed potential difference across the interface is too low by a factor greater than two. Indeed there is every reason to believe that this factor should be even greater than two, since the value reported by Wolf is undoubtedly too low due to an association of butyric acid molecules when dissolved in benzene. The effect of this association is to lower the electric moment of a dissolved molecule. It was previously mentioned in the case of benzoic acid[3] and in the case of cyclohexane carboxylic acid.[4] Since the group moment[5] of the C – OH linkage is 1.7 and that of the C=O linkage is 2.8 a simple spatial consideration for the carboxyl group indicates that its characteristic moment will be greater than the difference between the moments characteristic of its components, that is, 1.1. In other words the moment of the butyric acid molecule may well be taken as being greater than $\mu = 1.1 \times 10^{-18}$ e.s.u., that is, approximately four times the value calculated from the potential difference data.

To cite a single other case, the change of potential difference when chloracetic acid is substituted in the interface for acetic acid can depend only on the value of the electric moment characteristic of the C–Cl linkage. In this way the value, $\mu = 0.5 \times 10^{-18}$ e.s.u., is found. However, the moment for methyl chloride is $\mu = 2.0 \times 10^{-18}$ e.s.u.,[6] so that again the moment calculated from the potential difference at interface data is too small by a factor of something like four. In fact, it seems that any electric moment calculated by a method similar to the one outlined by Rideal will be too small by a factor of this order of magnitude.

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[1] Rideal: "Surface Chemistry" (1926).

[2] Wolf: Physik. Z., **31**, 277 (1930).

[3] Williams and Allgeier: J. Am. Chem. Soc., **49**, 2416 (1927).

[4] Williams: J. Am. Chem. Soc., **52**, 1831 (1930).

[5] Williams: J. Am. Chem. Soc., **50**, 2350 (1928).

[6] Sänger: Physik. Z., **27**, 556 (1926).

Frumkin and Williams[7] have recently sought to account for the reason, or reasons, why the electric moment of a molecule cannot at present be calculated from potential difference at interface data. Four possibilities were suggested, as follows:

1. Incomplete orientation of the molecules at the interface.
2. A disturbing influence of the neighboring water molecules or ions.
3. Differential nature of the measurements of potential difference.
4. The polarization of the oriented molecules by the neighboring molecules, assuming the orientation to be always complete.

It was shown that there are certain objections to most of these possibilities. If, however, the oriented molecules are polarized by the presence of the neighboring molecules a dielectric constant of the order of magnitude three or four instead of unity might be accounted for. Since the equation relating electric moment and potential difference involves the assumption that the dielectric constant of the molecules at the interface is actually unity it is evident that a higher dielectric constant of magnitude three or four would account for the larger part of the discrepancy. It will, however, be very difficult to make any statements concerning the dielectric constant of the surface layer, so in order to accept this as an explanation experimental data must be made available.

Careful examination of factors 1 and 2 indicates that if they are operative the potential difference at the interface should be a function of temperature. Furthermore, it follows from our modern ideas concerning the factors which contribute to the dielectric constant of a system that if the oriented molecules are polarized by the presence of neighboring solvent molecules this polarization, and therefore the potential difference at the interface, calculated for equal amounts adsorbed, should be practically independent of temperature. Therefore, if data giving the temperature coefficient of this potential difference were made available it should lead to an elimination of either possibilities 1 and 2 or of possibility 4. We sought to obtain data of this character.

In view of papers published by Kenrick[8], Guyot[9], Frumkin[10], Bühl[11] and Garrison[12] it appeared as if this might be achieved, since in these articles there are described three distinct methods to measure the interfacial potential difference. However, the general agreement between the results of these methods and the agreement between the results of different observers leaves much to be desired. In our experiments we used both the method of Kenrick and the method of Guyot and Frumkin, and many modifications of each in the attempt to reproduce the results which have been reported.

The experimental arrangement of Kenrick makes use of a single vertical glass tube down the inner surface of which the reference liquid is allowed to flow. The second liquid is passed from a fine glass tip in the form of a narrow jet down the axis of the tube. The two solutions are connected through calomel electrodes to a quadrant electrometer which is calibrated to read the electromotive force of the cell. This method is claimed by Kenrick and also by Frumkin to give very satisfactory results in the case of inorganic electrolytes and readily soluble derivatives of shorter chain hydrocarbons. There are however, several serious sources of error, namely

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[7] Frumkin and Williams Proc. Nat. Acad. Sci., **15**, 400 (1929).

[8] Kenrick: Z. physik. Chem., **19**, 625 (1896).

[9] Guyot: Ann. Phys., (10) **2**, 506 (1924).

[10] Frumkin: Z. physik. Chem., **111**, 190 (1924); **116**, 485 (1925); **123**, 321 (1926).

[11] Bühl: Ann. Physik, (4) **84**, 211 (1927); (4) **87**, 877 (1928).

[12] Garrison: J. Phys. Chem., **29**, 1517 (1925).

1. Streaming potential developed by the second liquid in case of dilute solutions.
2. Balloelectric effect associated with the formation of fine drops and spray by the liquid jet.
3. Liquid-liquid junction potentials.
4. Electrostatic effects of unknown origin and magnitude.

We have demonstrated experimentally that these liquid junction potentials may easily be as large as the potential difference across the interface which has been reported in various cases.

A second method, which is subject to less error than the method just described, was developed by Guyot and by Frumkin for determining the change in the potential difference when capillary active substances are present. In this arrangement a stationary liquid surface is used. A platinum electrode which has been coated with a radioactive material is placed directly above

TABLE I

Solution	Conc. N.	Kenrick Dropping Electrode	Frumkin Dropping Electrode	Garrison Condenser Method	Bühl Dropping Electrode	Authors Ionization Method (Modified)
H_2O				+40	−5.5 ±0.5	−9
KCl	1.0		−2			−56
KCl	0.1			+70		
KBr	1.0		−10			−82
KI	1.0		−34	+125		
KSCN	1.0		−57	+70		
NaCl	2.0		−4			
NaCl	1.0		− 1	+80	±0	
HNO_3	1.0	−53	−48	+265		
HCl	2.0		−55	+100		
HCl	1.0	−29	−23	+185		−50
HCl	0.5			+230		
HCl	0.1	− 8		+170	±0	
H_2SO_4	1.0		−13.5			
KOH	1.0		0			+158
NH_4OH	1.0		+78			

this surface. The ionization of the air produced in this manner is sufficient to permit a determination of the potential difference between this air electrode and the body of the liquid. The activated electrode is directly connected to the isolated pair of quadrants of an electrometer, while the liquid is joined by a potassium chloride bridge to a calomel electrode connected to the other pair of quadrants.

In our experiments with the method of Guyot and Frumkin we were successful only to the extent of a partial agreement with the results obtained by these investigators. We did not obtain the same absolute magnitudes, but values which were shifted by a more or less constant factor from them, in spite of the fact that we tried to compare them to the same reference solution. In Table I we have shown a comparison of the results of the various investigators with our own for several solutions of inorganic electrolytes.

Thus it appears that before we can hope to calculate electric moments of molecules from interfacial potential difference data a number of experimental difficulties will have to be solved. It appears that in addition to the possibility already mentioned, a difficulty due to the differential nature of the measurements of potential difference, there may be involved other factors in the experimental procedure which have not been properly controlled. To determine the value of an electric moment it will certainly be necessary to know the *single* potential difference. It seems probable that any experiment will always give a differential effect which is related to a layer of pure solvent molecules or to some other quite arbitrary zero point. Represented schematically the cell whose potential difference is measured is as follows:

Pt + Radioactive Material	Air	Molecule AB (Conc. C, in conducting solution)	Hg_2Cl_2 KCl (sat'd)	Hg

The measured electromotive force of such a cell will evidently not be the single potential difference but a combination of several potential differences; in other words it appears that the potential difference observed will be related to some arbitrary, even if practically constant, reference. Thus, our values differ from those of Frumkin, although we tried to reproduce them exactly. We believe that this difference can be explained, (at least in part), by the difference in radioactivity of the substances used to ionize the air in the two experiments.

Air	Molecule AB (Conc. C, in conducting solution)

It appears also that even had we used the same radioactive substance in exactly equivalent amount we could have reproduced the earlier results only if we could have adjusted the electrode to exactly the same height above the surface in our experiments. It is evident from Fig. 1 that the measured electromotive force is a function of the distance of any given radioactive electrode from the stationary liquid surface. For comparable results it will always be necessary to use equivalent amounts of radioactive materials on an electrode which is always accurately adjusted to a predetermined height. These results will not be absolute in nature, rather they will be referred to a constant which appears at the present writing to be indeterminable.

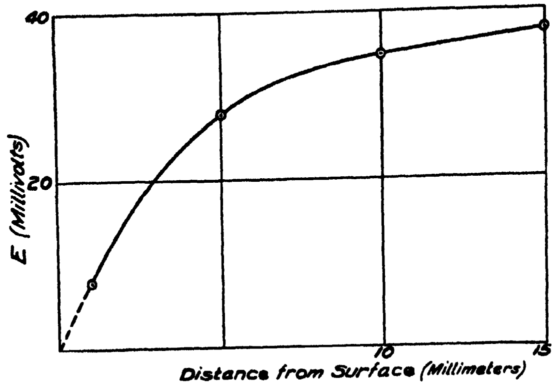

FIG. 1

Variation of potential with distance of electrode from surface of solution.

It should not be necessary to mention that serious errors may affect the results if the apparatus and leads to the electrometer are not properly shielded and insulated. In our experiments every known precaution was taken.

As stated, our original intention was to study the temperature coefficient of the potential difference at several interfaces to see if there could be eliminated any of the possible reasons why the electric moment of a molecule cannot at present be calculated from interfacial potential difference data. Because of the time involved in the study of the various experimental methods described in the literature which do not give concordant results and in the construction of an apparatus which does give a reproducible result our data on this particular point are too meagre to report at the present time except to say that there appears to be a real temperature effect. We are not at present willing to commit ourselves as to whether this temperature effect is due simply to the change in the junction potentials involved, or is really caused by either a decrease in the degree of orientation of the molecules at the interface as the temperature is increased or a change in the disturbing influence of the neighboring water molecules or ions.

We do feel it to be worth while, however, to point out that in spite of the tremendous difficulties involved in this type of measurement something has been and is being accomplished by workers in this field. It has been shown that there is a striking difference in the *order of magnitude* of the electric moment calculated from the potential difference data and that calculated according to the now familiar dielectric constant methods, yet there are a number of marked parallelisms between the results of the two types of study. Both indicate very definitely that polar molecules of the organic type are made up of polar parts and non-polar parts. In the simpler molecules which have but a single polar group the length of the hydrocarbon chain appears to have little or no effect. These are conclusions whose importance need not be discussed further.

Agreement is also generally found when the conclusions concerning the sign of the charge on definite linkages is considered. Thus in the case of the carbon to oxygen linkage the carbon is charged positively with respect to the oxygen; in the case of the carbon to chlorine linkage the carbon is charged positively with respect to the chlorine; and in the case of the carbon to nitrogen linkage the carbon is positively charged and the nitrogen negatively charged. This conclusion is more definite from potential difference data than it is from electric moment data in the case of the linkages to oxygen and nitrogen because of the structures which have to be assigned to the water and ammonia molecules and to what may be considered to be their derivatives. The two valence bonds of the oxygen atom are not extended as has usually been assumed in the discussion of molecular orientations at interfaces, but make an angle of considerably less than 180° with each other. Thus if the alcohol, ROH, be considered to be oriented at the interface water-benzene the oxygen atom is the hydrophilic part of the molecule just as it has always been considered to be in the case of ether molecules, ROR′. Likewise, the three valences of the nitrogen atom are directed toward the corners of a tetrahedron with the nitrogen atom situated at the apex.[13]

If, however, allowances are made for the stereochemistry of the various atoms involved it is found that the order of magnitude of the electrical effects for the alcohols, ketones, ethers, esters, and amines is relatively the same as the dipole effects, in order. The influence of the change when bromine is substituted for chlorine, or iodine is substituted for bromine is readily comparable in both cases. From the remarks made in an earlier part of this article it is evident that the effects in the case of the acids cannot be compared because of the difficulty in obtaining electric moment data for this type of compound.

Before leaving this particular discussion it is well to note that the interpretation of the electric moment data is not as simple as might be wished because the molecules must be considered as non-rigid in practically every case. There is even in some cases evidence in favor of rotation about valence bonds which is quite unrestricted by other parts of the molecule in the case of both aliphatic and aromatic derivatives. The electric moment as measured must be considered to be an average moment, and nothing more. If it were possible to calculate the electric moment of a molecule from interfacial potential difference data this moment might be quite different because it could only be the moment of a molecule fixed in position because of the proximity of its neighbors.

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[13] See Debye: "Polare Molekeln," (1929); Sack: Ergebn. exakt. Naturwiss., **8**, 307 (1929); Williams: Fortschritte Chem., Physik, physik. Chem., **20**, und No. 5. (1930); Chem. Rev., **6**, 589 (1929).

There is another comparison between data from two types of study which make it appear that, at least in a relative way, the interfacial potential difference data which now exist in the literature are not without significance. If one compares the results of a study of the electrocapillary curves with those obtained from the potential differences measured according to the methods described above there is a definite, even if qualitative, agreement between them. Experiments show[14] that the position of the maximum of the electrocapillary curve changes strongly with the composition of the solution. Gouy showed that these effects could be explained on the basis of an adsorption of ions or molecules at the interface, and it has developed that considerable information about the orientations of molecules at this mercury-water interface may be obtained by observing the changes produced in the rising and falling branches of the curves obtained when the interfacial tensions are plotted against the applied potentials. The observed shift in the maximum of this curve indicates the existence of an adsorbed layer of molecules which produces a potential difference between the mercury and the solution, such that if the positive end of the molecule is turned toward the mercury the maximum will be shifted in one direction, and if it is turned toward the water the maximum will be shifted in the other direction. Since the potential difference data discussed and described in this article are attributed to an adsorption of these compounds at the air-water interface and since this adsorption gives rise to similar electric effects Frumkin[14] has compared the results of the two types of study and has found it necessary to assume that at the mercury-water interface there exists the same orientation which is known to exist at the air-water interface. This means again that the polar group is attracted by the water and the non-polar group by the less active substance.

The result of this comparison of data may be stated by saying that except in the cases where there is reason to believe that there exists a specific interaction between the mercury surface and definite constituents of the molecules in question there is good agreement between the conclusions which have to be drawn from the data in both these cases. It seems probable, too, that when the potential differences across the air-water interface can be measured more accurately this agreement will become even better.

It might be mentioned that it would perhaps have been easier to study the effect of a change in temperature on the position of the maximum in the electrocapillary curve in order to account for the reason, or reasons, why the electric moment of a molecule cannot be calculated from interface potential difference data. It was because of the fact that these specific interactions between the mercury surface and certain constituents of molecules had been previously recognized and would have complicated the situation that measurements at the mercury-water interface were not made. Furthermore, in that event it would have been necessary to reason by analogy rather than by direct inference from the experimental data which were made available. Measurements of this type are now being made upon systems designed to avoid these specific interactions.

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[14] Frumkin: Colloid Symposium Annual, 7, 89 (1929).

Finally, it is clear that if we are to increase our knowledge concerning the orientation and structure of molecules at interfaces the electrical properties of these interfaces must be studied as a function of temperature. While a method which seems to be suitable for this study in the case of the mercury-water interface is available it appears that considerable work still remains to be done before a technic will be developed which can be depended upon to give reproducible and comparable results in the case of the air-liquid interface. Two methods, the air ionization method of Guyot and Frumkin, and the electrostatic method of Garrison can be considered to be correct in principle, but as yet they have not given results in any agreement whatsoever, even at a single temperature.

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SOME UNUSUAL PROPERTIES OF COLLOIDAL DISPERSIONS[1]

BY R. V. WILLIAMSON

We have been studying the viscous and plastic properties of dispersions for several years in order to increase our knowledge of their structure. During this time we have collected several dispersions that show rather striking characteristics when caused to flow under different conditions. The structural characteristics of these dispersions are only partially known, but their flowing properties are of considerable interest to the manufacturer of colloidal dispersions, and a description of them may also interest those who are studying the problem of colloidal structure in a theoretical way.

The Flowing Properties of Paints and Similar Suspensions. The paint manufacturer has known for a long time that the practical flowing and brushing behavior of paints cannot be estimated for their viscosities as ordinarily determined. This fact may be demonstrated with dispersions made by grinding 11 to 14 parts by volume of zinc oxide in 100 parts of alkali-refined raw linseed oil, blown linseed oil, and blown linseed oil thinned with turpentine until it has the same viscosity as the raw oil. The dispersions in the raw oil and in the thinned blown oil have the same apparent viscosity when stirred or when allowed to flow through an ordinary viscosity cup. Blown linseed oil is considerably more viscous than the raw oil; and the blown oil dispersion similarly exhibits a very much higher apparent viscosity than the other two.

The flowing characteristics of these dispersions may be compared by painting glass plates with each of these dispersions, placing small cylinders (approximately one centimeter high and one-half centimeter inside diameter) open at both ends on the freshly painted glass plates, filling each cylinder with the paint that was used to paint the glass plate upon which the cylinder rests, and then gently raising the cylinder and allowing the paint to flow out. The raw-oil dispersion flows out to a much smaller area than the other two although its apparent viscosity is comparatively low. The blown-oil and thinned blown-oil dispersions flow out to approximately the same area in spite of the difference in the viscosities of the two dispersions. The time required for the blown-oil dispersion to flow out is greater, however, than that required by the thinned blown-oil one.

If the apparent viscosities of these dispersions are determined at different rates of flow through a capillary tube, the raw-oil dispersion shows a very high apparent viscosity at low rates of flow, but at high rates of flow its apparent viscosity is about the same as that of the thinned blown-oil dispersion. In other words, this dispersion shows marked plasticity. The other two dispersions do not show much if any change in viscosity at different rates of flow; *i.e.*, they flow like ordinary viscous liquids.

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[1] Contribution No. 39 from the Experimental Station, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware.

Photomicrographs of the specimens reveal a highly flocculated condition of the particles in the raw-oil dispersion, whereas the particles are highly dispersed in the other two dispersions. The areas covered by the dispersions as they flow out on the painted glass plates appear to be a function of the size of the flocculates. The degree of plasticity of the dispersions is also directly related to the sizes of the flocculates. One may say, therefore, that the flowing properties of a dispersion can be estimated from its plastic properties.[2] This is qualitatively true, but unfortunately scientists have not been able to find a satisfactory method for quantitatively expressing the plastic properties of dispersions.

A mental picture of some of the factors that determine the areas of the flow-outs may be drawn as follows: As the oil film advances the largest flocculates settle to the bottom first, and the friction on the glass plate prevents them from advancing farther. The smaller flocculates, however, are carried still farther. Finally the film advances until the friction of the smallest flocculates between the glass plate and the air-oil surface is great enough to overcome the "head" or stress due to the thickness of the oil film. If the forces of flocculation are sufficiently great to prevent the flocculates from being broken into smaller ones under this stress, the advance of the particles in the film is stopped.

The control of the plastic characteristics of paints is important to the paint manufacturer because to a large extent they determine the character of the surface of the paint film. In enamels, the plasticity must be very low so that brush marks and any uneven surface characteristics will disappear, and the paint will flow out to a mirror-like surface. In flat wall-paints, printing inks, and paints for printed linoleum, a certain amount of plasticity is essential.

Thixotropic Dispersions. The term thixotropy has been used by Freundlich[3] and others to describe that property of dispersions that enables them to change repeatedly from a gel form to a liquid form under the stress of agitation and then to revert to the gel form again when allowed to remain at rest. The first thixotropic dispersion that I observed was prepared by Marion Veasey at the University of Wisconsin in 1922. This was an aluminum hydroxide dispersion. Freundlich and his co-workers have described the conditions for preparing thixotropic dispersions of ferric oxide and aluminum hydroxide. I have observed several thixotropic dispersions of pigments. One of these was presented to me by C. K. Sloan of this laboratory. It is a dispersion of gas black in petroleum hydrocarbon which contains an organic dispersing agent. This dispersion remains very fluid for an hour or more after shaking, but it sets to a solid gel in a few hours. The time required for gelation can be shortened by reducing the amount of volatile vehicle until the dispersion will set immediately after shaking. This dispersion has been kept in the laboratory for a year, and the thixotropic property has been demonstrated many times without any apparent change in this property of the dispersion.

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[2] For further discussion of this point, see Williamson: Ind. Eng. Chem., **21**, 1108; Williamson, Patterson, and Hunt: 1111 (1929).

[3] Freundlich: Kolloid-Z., **46**, 289 (1928).

A dispersion with similar properties may be prepared by mixing zinc oxide (such as is used as a paint pigment) with gasoline in the proper proportions. If such a dispersion, contained in a small can, is shaken vigorously, it produces a sound resembling that produced by a very fluid liquid under similar circumstances. The dispersion does not flow out, however, if the shaking is stopped, the lid immediately removed, and the can turned bottom side up. In this case, the effect is probably due to the highly flocculated condition that results from the poor wetting of the zinc oxide by the vehicle. This effect can be completely changed by adding a few drops of some good wetting agent, such as blown linseed oil. The dispersion then remains perfectly fluid after shaking, but the pigment settles rather rapidly to the bottom of the container.

Inverted Plasticity. The thixotropic dispersions described above are examples of highly plastic dispersions. Such dispersions are characterized by a very high apparent viscosity when stirred slowly and a lower viscosity when stirred rapidly. Several dispersions have been brought to my attention that show an inverted form of plasticity, compared to that described above. These dispersions flow readily when stirred slowly, but become quite stiff when stirred rapidly. I have used the term "inverted plasticity" in referring to this property. Victor Cofman called my attention to the fact that a dispersion of corn-starch and cold water in approximately equal proportions by weight shows this property to a marked degree. A striking demonstration can be made by inserting the finger into the dispersion, moving it around slowly to show the fluid character of the dispersion, and then jerking it out quickly, whereupon one receives the impression that the dispersion has solidified around the finger. If the concentration is right and the beaker is held firmly on the table, the whole mass of the dispersion will tend to be lifted as a solid. As soon as the violent agitation is stopped, the whole mass becomes fluid again.

The peculiar properties of this dispersion can also be demonstrated by replacing the cylinder on a Stormer viscometer with a double-pronged stirrer[4] and determining the rates of stirring of the dispersion with different weights on the stirring device. For ordinary viscous liquids or dispersions the rate of stirring is proportional to the load on the stirring device. If the concentration of the starch dispersion is adjusted properly (approximately 1:1 by weight) and the same test is applied to it, the stirrer rotates at a uniform rate with only the weight of the pan on the stirring device. If a thousand-gram weight is added to the pan, the stirrer continues to rotate at the same rate.[5]

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[4] The Stormer viscometer was modified in this way by Booge and Steinbring in the duPont Laboratories.

[5] The properties of this dispersion are described in greater detail in a paper with Heckert: Paint Oil Chem. Rev., 89, 9 (1930).

The same property has been found in a number of dispersions of ordinary paint pigments in organic vehicles by Heckert and Sloan at the du Pont Experimental Station. Since the effect appears only within certain concentration limits, it is probably related to the increase in volume that occurs when granular masses are deformed, owing to differences in the relative pore-space for different arrangements of the grains or particles. This phenomenon was named "dilatancy" and explained by Reynolds.[6] Inverted plasticity is not, however, determined simply by the relation of the volumes of dispersed solid and vehicle, for it occurs only in those dispersions in which the vehicle has a high dispersing action on the particles or, in other words, wets the particles well.

Sodium Silicate Dispersions. The viscous, plastic, and elastic properties of sodium silicate dispersions vary greatly with the relative proportions of sodium, silica, and water. A dispersion that exhibits properties similar to the inverted plasticity described above can be prepared by evaporating the water from an ordinary water-glass solution until the proper concentration of sodium silicate is reached. The proper concentration can be readily determined by removing a piece of the dispersion from the mass by means of a spatula, drawing it out very slowly with the hands, and laying it on the table to show that it has no tendency to return to its original shape, and then cutting a fresh piece from the original dispersion, rolling it into a ball, and throwing it to the floor with considerable force. If it has a suitable concentration, it bounces from six to ten feet in the air. If an attempt is made to stretch the ball rapidly, it breaks with the conchoidal fracture characteristic of a non-crystalline solid. Different types of flow are shown by other sodium silicate dispersions. For example, one may prepare a dispersion (with a higher ratio of sodium to silica and a lower proportion of water) which appears to flow under low stresses in much the same manner as the one described above, but which behaves quite differently under high sudden stresses. The similarity as well as the difference in properties of the two dispersions can be shown by wrapping a sample of each dispersion in tin-foil and applying the following tests. If the samples are squeezed gently between the thumb and finger, both of them feel soft and flow slowly and in much the same manner. But if the samples are thrown to the floor, the difference in properties is revealed. The first sample bounces like a rubber ball, and the second sounds like a brick instead of the soft sodium silicate dispersion. If the sample that bounces is subjected to a sudden pull, it breaks with a conchoidal fracture, whereas the one that strikes like a brick stretches like a good grade of pulling taffy.

A slight modification of the above demonstration serves very well to illustrate how much alike different dispersions may be under one set of conditions and how different under another. For example, the two sodium silicate dispersions described above may be placed in rubber bags made from toy balloons and a third specimen added containing a paste of ordinary molding clay and water. If the concentrations of these dispersions are properly adjusted, they all feel soft and deform to about the same degree when squeezed gently. But when they are thrown to the floor, the first bounces like a rubber ball, the second does not bounce but sounds like a rock hitting the floor, and the third squashes like a bag of wet meal.

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[6] Phil. Mag., 20, 496 (1885); Proc. Roy. Inst., (1886); "Scientific Papers," 2, 203, 217 (1901).

The first sodium silicate dispersion exhibits the property of inverted plasticity described above in connection with starch and water suspensions. Attention was there called to the similarity of the conditions of concentration necessary for producing inverted plasticity and "dilatancy". The same similarity exists in the case of the sodium silicate dispersions, for the property is noticeable only within a limited range of concentration. Attention was called, however, in the case of the starch and water suspensions to the difficulty of accounting for the property of inverted plasticity on the basis of the volume relation of starch and water alone, because the property is specific for given liquids. The difficulty is even more pronounced in the case of the sodium silicate dispersion, for the dispersion has no obvious suspended particles. Also, the second sodium silicate dispersion is several times as concentrated as the first, yet it does not exhibit inverted plasticity.

I am indebted to James G. Vail of the Philadelphia Quartz Company for the sodium silicate demonstrations.

Liquefaction of Viscose Gels by lowering the Temperature. Most materials become more fluid as the temperature is raised and become solid or freeze when the temperature is lowered sufficiently. Viscose is rather unusual in this respect inasmuch as freshly prepared viscose sets to a gel within a few minutes when heated to the temperature of boiling water and liquefies again when placed in an ice bath. Liquefaction of the gel does not take place, however, unless it is placed in the ice bath immediately after gelation occurs. The phenomenon is probably due to changes in hydration of the components of the dispersion brought about by lowering the temperature. If the chemical changes that produce gelation proceed too far, the changes in hydration produced by lowering the temperature are not sufficient to redisperse the gel again. It is essential that only a small amount of viscose is used for demonstrating this property so that the time required to change the temperature of the whole mass is short. We ordinarily use about five cubic centimeters contained in a test tube. The test tube is placed in a glass vessel that contains boiling water. The viscose is stirred with a glass rod, and the heating is continued until the material shows a definite crack that does not flow together when the stirring rod is drawn through the material while the end of the rod is in contact with the wall of the test tube. This is considered to be the point of gelation. If the gel is then taken out and immediately placed in an ice bath, it returns to a fluid condition.

Summary

A number of experiments are described to show the marked changes in the plastic and elastic properties of dispersions which may be produced simply by changes in temperature or in the magnitude and the rate of application of stresses. The experiments may be useful to the manufacturer of colloidal materials because they illustrate some of the unexpected results that may occur from simple changes in the physical environment of the materials. They should also be useful to those interested in the fundamental study of structure in colloidal dispersions because they furnish a number of facts which must be explained by any comprehensive theory of colloidal structure.

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SOME CHEMICAL REACTIONS OF COLLOIDAL CLAY

BY RICHARD BRADFIELD

At the first Colloid Symposium seven years ago, the author had the privilege of presenting a paper on the same subject[1] as the above. In preparing this paper the first was reread with considerable interest and amusement. A friend, noted for his frankness, once remarked that the best part of the earlier paper was the discussion which followed! As this discussion was reread I wondered if our committee had acted wisely in abandoning the policy adopted by Professor Mathews of publishing at least a résumé of the discussions in the Symposium Annual. An opinion the earlier paper shared by many was that it was rather futile to attempt to obtain an understanding of the reactions of a substance as complex as a clay. "Simple" substances like silicic acid, aluminum and iron hydroxides, pure carbon, and pulverized soil-forming minerals were suggested as being much more suitable objects of study.

The author was not completely indifferent to this advice and at times has used all of these "simple" substances in comparative studies with clays; nor was he convinced that it was wise to abandon clays completely for these simpler systems. The economic importance of clays to both agriculture and industry seems sufficient to justify some study of this material in spite of its complexity. Most comparisons of the behavior of natural clays with these simpler, supposedly similar substances, have served but to show how different the two really are. For every property found in common, several can be found in which they are very different. This has led to the feeling that the only way to find out about clays is to study clays. Synthesis is often the capstone of a chemical research problem but analysis logically precedes it. If we learn enough about the behavior and properties of clays we may eventually be able to make synthetic imitations. But first we must know a little more about what we are trying to imitate.

The term clay means very different things to different people. To the soil scientist a clay is that inorganic fraction of the soil whose particles are less than 2 microns in diameter. Colloidal clay is that fraction of the clay whose particles have an effective diameter of less than 100 millimicrons. Since it represents a fractionation based solely on size of particle it may be applied to fractions which differ greatly in both chemical composition and in mineralogical make up.

Since the classic work of Odén and Svedberg many attempts have been made to determine the size-distribution of clays. The chief difficulty encountered is to secure suspensions of stable unit particles. Most of the clay exists naturally, fortunately for the farmer, in the form of rather stable aggregates. The various methods of deflocculation commonly used were not

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[1] Bradfield: Colloid Symposium Monograph, 1, 369 (1923).

100 per cent efficient and consequently the older mechanical analyses represented neither the size-distribution of the naturally occurring aggregates nor of the unit particle, but something in between these extremes.

Recent studies of base-exchange phenomena and their effect upon the electrokinetic potential of clays, which will be discussed later, have pointed out the way to obtain more efficient deflocculation. It is now quite definitely proven that the amount of colloidal material in clays is much larger than earlier workers believed. Most of them, Schloesing, Ehrenberg, Gedroiz, et al, felt that the amount of truly colloidal material in clays was at most only a few per cent. Recent work has revealed clays with 80-90 per cent colloidal material, while from 20-50 per cent is quite common. In fact there is a decided tendency to regard all clay particles under 2 microns in diameter, as defined by the International Society of Soil Scientists, as being colloidal. The Bureau of Soils' workers were the first to suggest that the limit should be placed at 1 micron. Joseph, working on African clays, came to the same conclusion. Some experiments made by DeYoung in the author's laboratory furnished strong evidence that practically all the particles, in certain clays at least, that are under 2 microns in diameter are in reality made up of aggregates which may be broken down to particles about 10-20 millimicrons in diameter by merely churning with distilled water, centrifuging out particles larger than 20 millimicrons by means of the supercentrifuge, resuspending the coarser particles in distilled water, recentrifuging, etc. The original purpose of this experiment was to prepare a series of fractions of clays with different specific surfaces and to study the absorptive power as a function of external surface. It proved a very easy matter to secure large quantities of clay with particles between 2000 and 10 millimicrons; but it did not prove possible to make satisfactory fractionations of this material. After 8-10 fractionations all of the original kilogram of clay with particles under 2000 millimicrons was reduced to a fraction with particles from 10-20 millimicrons in diameter.

The amount of stable particles between 1000 and 20 millimicrons was negligibly small in this clay. The 2-5 microns fraction was very stable and easily washed free from all smaller particles. It possessed, however, none of the properties usually associated with clays but was decidedly silt-like in nature. Thomas, working in Utah, and Joseph, working in Africa, have observed that the smallest clay particles in the samples studied by them were of the same order of magnitude as those found above. The almost total absence of particles of the intermediate sizes may prove quite significant if found to be generally true. It is hoped that the investigation can be extended to other clays using an improved technique.

Shape of Particles. A large proportion of the particles of most clays are plate-like in form. The stream lines observed when a clay sol is gently stirred is evidence of this. The particles can be oriented also by means of an electric field. The number of particles visible in the ultramicroscope can often be increased from 20-40 per cent by applying an electric field perpendicular to the direction of the illumination. These oriented sols are strongly doubly refracting, the amount and sign of the double refraction varying with the nature of the cation saturating the clay. The surface of clays is tremendously increased as a consequence of this plate-like shape. Variations in plasticity may frequently be associated with the extent of this plate-structure development.

X-ray and Chemical Analysis. Results obtained by the X-ray analysis of clays were discussed before this symposium last year. Kaolinite which many used to consider the predominant mineral in clays seems to be rather rare in agricultural soils. Minerals of the nontronite, beidellite, and montmorillonite types seem to be much more abundant. Chemical analyses of the colloidal fraction of clays have revealed the rather interesting fact that clays formed under similar climatic conditions tend to be very much alike in spite of great differences in the origin and nature of the parent material. The colloidal fraction of most of the soils of the corn belt regions of this country has a silica-sesquioxide ratio of about 3 to 1. Other ratios are found, of course, but this one is most common. As we approach the tropics the proportion of sesquioxides increases and in extreme cases, the so-called lateritic clays, the silica disappears almost completely. All gradations between these extremes can probably be found. These considerations render extremely improbable the view held by some, that there is a single base-exchange complex or a single alumino-silicate responsible for soil acidity phenomena.

Thus far an attempt has been made to portray the physical and chemical make-up of some of these colloidal clays as a preface to a discussion of some of their chemical reactions. All the studies to be considered were made on the colloidal fraction of clays with particles all under 100 millimicrons which apparently were rather instable and capable of being broken down easily into particles from 10-20 miilimicrons in diameter. These particles are crystalline and are for the most part plate shaped. Mineralogically they seem to belong to either the montmorillonite or beidellite group.

Cation Exchange Reactions. The long-known ability of soils to exchange a certain definite amount of their cations for the cations of neutral salts is associated largely and in some soils almost exclusively, with this colloidal fraction. This exchange capacity varies commonly from 0.30-1.00 milliequivalents per gram. The clays differ from the synthetic permutits, with which they are so often compared, in that a much smaller percentage of their total cations are easily exchangeable. In the permutits which have the general formula 1 base.$Al_2O_3-3SiO_2.xH_2O$ almost 100 per cent of the cations present can be rather readily exchanged for the cations of a neutral salt. This corresponds to from 3.2 to 4.5 milliequivalents per gram depending upon the amount of hydration. The total amount of cations in the permutit and clay are almost identical. The exchangeable fraction constitutes then from but 10-30 per cent in clays ordinarily in comparison with 95-100 per cent in permutits.

This difference is commonly explained by assuming a much more porous structure in the case of the permutit, the so-called permutoid structure of Freundlich in which the entire interior surface is readily accessible to the ions of the common salts. The clay particle is apparently denser in structure and the rapid exchange of ions is limited to those situated near the surface. Given sufficient time, suitable concentrations, and higher temperatures, the exchange can go to completion also in the case of certain closely related ions which are capable of fitting into the crystal lattice of the particle, as was shown over 50 years ago by the studies of Lemberg.

Kelley[2] has found that the percentage of readily exchangeable cations in a bentonitic clay could be greatly increased by prolonged grinding. The effect of the grinding was apparently due to the opening of fresh surfaces. The additional base obtained was largely Mg. There is some evidence that this may be rather generally true. Ca and H on the other hand constitute the largest proportion of the exchangeable cations of the soils of the humid regions. In the alkaline soils of arid regions Na appears in the place of H and, in extreme cases, of Ca also.

The proportion of total Ca which is readily exchangeable is usually quite high, in many cases almost 100 per cent, indicating that it may be the product of a secondary exchange reaction rather than a part of the surface of the original particle. The fact that Ca occurs in the drainage waters of our soils of the humid region in greater abundance than the other cations, makes such an hypothesis probable.

Acid Clays. In humid climates any reserve of $CaCO_3$ which may have been present in the soil material is eventually leached away. After this reserve is exhausted the bases on the surface of the colloidal particles are gradually replaced by hydrogen ions supplied by the carbonic and other acids which are formed largely as a result of bacteriological activities. The extent to which this replacement of the basic ions by hydrogen ions has proceeded is a measure of the degree of weathering of the clay. Natural clays are found in which exchangeable hydrogen constitutes over 60 per cent of the total exchangeable cations. The division between exchangeable and non-exchangeable cations is not an extremely sharp one but in most cases it is sufficiently well defined that comparable values can be obtained by very different replacement methods. Almost identical values can be obtained, for example, by extracting the clay with tenth-normal solutions of strong acids, or normal solutions of appropriate neutral salts. Within reasonable limits the amount of cations replaceable is independent of the concentration of the replacing solution provided the extraction is continued to completion.

Electrodialysis. If most clays are subjected to electrodialysis a rather definite quantity of bases can be removed. The endpoint is usually rather sharp. The amount removed is found to be identical with that which can be removed by the acid or neutral salt extraction methods. The resulting clay is saturated with hydrogen ions. It is free or practically so from soluble salts and non-colloidal acids. Any ion which may have been present which was small enough to pass through a parchment membrane has been removed by the prolonged application of the electrical potential. This electrodialyzed colloidal clay represents an attempt to obtain a simpler system by methods which are not sufficiently drastic to cause any deep-seated change in the colloidal particle. As evidence of this, it has been found possible to put an electrodialyzed clay through a cycle of chemical reactions, for example, to neutralize it with $Ca(OH)_2$, replace the Ca by prolonged leaching with a neutral NaCl solution, and then electrodialyze again, obtaining a product apparently identical with that with which we started. It has the additional advantage that it can be brought easily to any desired degree of saturation with any of the important cations by the addition of the proper amount of the appropriate hydroxide.

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[2] In a paper presented before Am. Soc. Agron., Chicago, Nov. (1929).

Characteristics of Hydrogen Clays. 1. Influence of the solid phase upon the hydrogen-ion concentration of clay sols.

It has been long known that the potential of the hydrogen electrode, when immersed in a suspension of a carefully washed acid clay, was markedly influenced by the concentration of the suspension. The colloid-free aqueous extract of such soil was frequently found to be almost neutral. In earlier studies on the acidity of a very acid colloidal clay it was found that the relationship between the pH value of the clay sol and its concentration was very similar to that observed with weak acids such as acetic.[3]

On the basis of these and other experiments the hypothesis was advanced that the bulk of the acidity found in soils was due to acids whose anions were of colloidal dimensions on using the terminology of Michaelis, to acidoids. As the clay used in these earlier experiments were natural clays, only 50 per cent of whose exchangeable cations were hydrogen, it seemed that further work should be done on the clays saturated with hydrogen ions. The studies served naturally to magnify the differences between the clay and its aqueous extract. With an electrodialyzed bentonite, for example, it has been found that while the clay-paste collecting on the membrane of an ultrafilter and containing about 10 per cent of oven dry clay had a pH value of 2.2 as measured with the quinhydrone electrode, the clear ultrafiltrate had a pH value of 5.2.

In a second experiment a 1.5 per cent electrodialyzed bentonite sol was placed in a collodion bag and the bag set in a volume of distilled water equal to that of the clay. After standing 24 hours so that equilibrium might be established it was found that the bentonite sol on the inside of the bag had a pH value of 2.8 while the water on the outside gave a pH value of 5.4. The hydrogen, quinhydrone, and antimony electrodes all gave pH values in satisfactory agreement, with these sols.

It is felt that the function of the membrane in these experiments was merely mechanical, preventing the diffusion of the colloidal clay anions. Any Donnan effect resulting from traces of any diffusible acids which might have been present would serve to decrease the differences in hydrogen ion concentration observed on the two sides of the membrane. Any other mechanism for separating colloidal clay from the medium in which it was suspended would probably give identical results. Similar results have been obtained by using centrifugal force for the separation. The differences in pH value between the clay thrown down and the supernatant liquid were not as great as in the case of the ultrafiltration experiments due to the fact that all of the clay particles could not be thrown down with the centrifugal force available. The simplest explanation of these observations is that a part of the hydrogen on the surface of the acid-clay particle is ionized and is far enough removed from the particle to act as an ordinary "free" hydrogen ion when brought in contact with the electrode, but these ions are restrained by electrostatic forces from moving farther than this distance.

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[3] Bradfield: J. Phys. Chem., 28, 170 (1924).

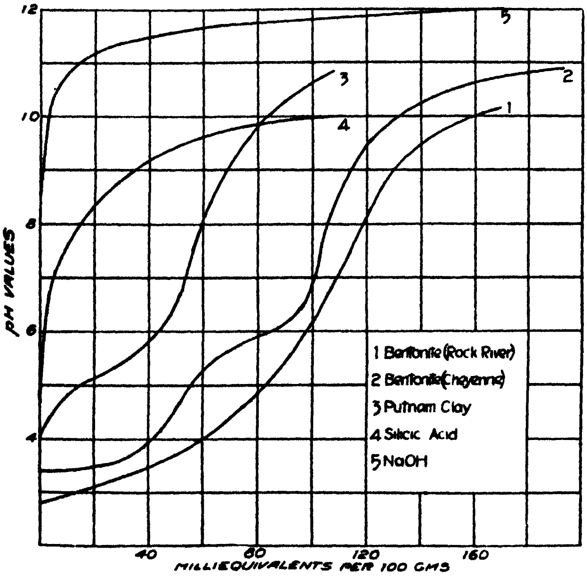

FIG. 1

Titratable Acidity of Electrodialyzed Clays. As has been shown earlier, even the natural clays give fairly distinct inflection points when titrated potentiometrically or conductometrically with solutions of standard hydroxides. The use of electrodialyzed clays tends of course to make these endpoints more distinct. A group of curves obtained by titrating 100 cc of 1 per cent electrodialyzed clay sols with 0.1 N NaOH using the hydrogen electrode are shown in Fig. 1. The curve for Putnam clay is of the type most commonly found in agricultural soils of the corn belt section. It resembles the monobasic type in having but one endpoint. This endpoint is not as sharp as those commonly obtained with simple monobasic acids. The reason for this, of course, is that these clay acids are very complex. For example, if we calculate the number of hydrogen ions that must be supplied by a particle with a radius of 10 mμ in order to account for the amount of NaOH neutralized up to pH 7.0, we find 7150. To account for this observed titratable acidity the particles of a true monovalent acid must have a radius of only 0.5 μ, a value much smaller than those observed.

One clay has been found, and so far as the author has been able to ascertain this is the only one reported which gives a curve having two rather distinct inflection points. (Fig. 1, curve 2). In appearance this bentonite from Cheyenne, Wyoming, was, superficially at least, very similar to the one from Rock River. The SiO_2 content of the two is almost identical—56 per cent. Minerals having two distinct types of crystal patterns have been found in bentonites. It may be that the dibasic character of the Cheyenne bentonite curve can be correlated with its mineralogical composition. The marked similarity between curves 2 and 3 at pH values above 6.5 indicates that these clays may have some constituents in common. A comparison of the silicic acid curve 4 with any of the clays shows how little they have in common and consequently how futile it is to attempt to obtain an understanding of the acidity of clays by studying "pure substances" which are so different from clays. The colloidal acids were prepared in a similar way, namely, the electrodialysis of their salts until all possible bases were removed. The curve for silicic acid shows a strong buffer action between pH values 9 and 11, indicating dissociation constants of the order of 10^{-10}: a value in satisfactory agreement with those found in the literature. It has, however, no buffer capacity in the acid region. Attempts have been made to prepare alumino-silicic acids by combining sodium aluminate and sodium silicate in the same ratios that they are found in clays, then converting the sodium salts into the acid by prolonged electrodialysis. The resulting product had no appreciable buffer action at pH values less than 7. Every other attempt made thus far to prepare synthetic substances analogous to clays has resulted in failure when subjected to this acidity test, even though the base-exchange reactions of clays and permutits are quite similar. Some have claimed that the differences in pH values of electrodialyzed permutits and electrodialyzed clays were due to the much finer particles of the latter. This might be true as far as pH measurements are concerned but the ability to neutralize NaOH in an acid medium should not be affected by particle size in substances as permeable to Na ions as are permutits, especially if sufficient time is allowed for the reaction.

Since clays which are made up predominantly of silicates and alumino-silicates are so different from any pure artificial substances we have been able to prepare, the question naturally arises as to whether or not other acid-forming substances might not be present in sufficient quantity to account for the results obtained.

The most common substances in clays other than SiO_2 that might contribute to the acidity are C, N, S, and P. The analyses of a series of electrodialyzed colloidal clays are shown in Table I. The bentonites are very low in all of these elements. The nitrogen content is not given but in clays it is usually only one-tenth as abundant as carbon. If one considers that all of the carbon is present as carboxyl groups, all the S as H_2SO_4, and all the P as

TABLE I

Content of Acid-forming Elements in some Typical Electrodialyzed Clays[4]

Colloidal Clay	C	S	P
1. Bentonite—Cheyenne. Finest	0.073	0.011	Trace
2. Bentonite—Cheyenne. Regular	0.198	0.005	Trace
3. Bentonite Rock River	0.055	0.019	Trace
4. Putnam	0.977	0.014	0.040
5. Putnam (H_2O_2 treated)	0.184	0.010	0.129
6. Susquehanna	0.667	0.014	0.065
7. Boone	0.566	0.015	Trace
8. Sharkey	0.591	0.025	Trace

H_3PO_4, which represents the maximum possible contributions of these substances to the acidity of the clays, we find that their combined acidity equals only about 10 per cent of that found by the titration curves. This seems to force us to the conclusion that the acidity of these clays is due to alumino-silicic acids. The differences in properties between the natural clays and the common synthetic alumino-silicates must be due to differences in structural arrangement.

Characterization of the Clay Acids. Many studies have been made of the quantitative factor of soil acidity, or amount of exchangeable hydrogen, but the intensity factor has received scant attention. The most obvious way of getting at this intensity factor is by the use of some expression which is analogous to the dissociation constants of ordinary weak acids, which the author has termed the apparent dissociation constant or, if expressed in the form of the negative logarithm, as the apparent pK value of the acid. It is obtained from the mass law equation:

$$pK = pH + \log \text{salt}/\text{acid}$$

At the point of half neutralization the last term becomes 0 and the apparent pK value is numerically equal to the pH value at that point. Such a treatment is of course not strictly rigid but it has the virtues of simplicity and usefulness and enables us to make comparisons with other acids.

By inspection of the titration curves we see that the apparent pK value of the Putnam clay is about 5.6, that of the Rock River bentonite 3.8, the Cheyenne bentonite 3.6 and 5.9, while that of silicic acid is of the order of 10.

It has been pointed out in an earlier paper that the relationship between the hydrogen ion concentration of a clay and its concentration is similar to that observed with weak acids such as acetic and that by the use of the simplifying assumption that the concentration of the unionized acid is equal to the total titratable acidity, the relationship can be calculated with a fair degree of accuracy from the mass law. The pK values calculated from the titration curve and from the pH concentration relationship are in satisfactory agreement.

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[4] Analyses obtained through the kindness of Mr. C. S. Schollenberger.

Distribution of a Base between Two Acids. If the apparent pK value has the significance attached to it above, it should be possible to calculate the pH value that would result when an acid clay is treated with an equivalent amount of the salt of a second acid of known pK value. Under these conditions[5] the relationship, $\frac{x}{1-x} = \sqrt{\frac{K_1}{K_2}}$ holds, in which x represents the amount of base combining with the acid, whose dissociation constant is K_1, and $1-x$, is the amount combining with the second acid. It is very easy to test this equation in the case of the colloidal clay acids because they can be separated from the second acid formed by merely centrifuging and titrating the clear supernatant liquid.

The results of a series of such experiments are shown in Table II. The agreement between the calculated and measured pH values are in most cases as good as one could expect. It is possible then, to calculate (1) the relationship between the pH value of clay suspensions and the concentration of such suspensions, (2) the pH values resulting when clay acids are treated with various increments of standard hydroxide solutions, and (3) the reaction resulting when clay acids of known combining weight are treated with the salts of acids of known pK value. This use of the pK value as an expression of the intensity factor of the acidity relations of clay acids is admittedly only an approximation but we are aware of no other method of treatment which enables us to predict as many of the reactions of clays.

TABLE II

Distribution of a Base between an Electrodialyzed Bentonite and Certain Organic Acids

Concentration of Salt Millimols per liter	Monochloracetic pK = 2.81				Lactic pK = 3.85			
	pH		Acid freed		pH		Acid freed	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
10	3·50	3·42	2.13	2.01	4·03	3·97	3·60	4·33
25					4·57	4·36	5·58	5·90
50	3·93	3·88	4·14	3·96	4·73	4·65	6.10	6.80
100	4.29	4·11	5·12	4·95	5·11	4·96	—	5·75

	Acetic pK = 4.74			
	pH		Acid freed	
	Found	Calcd	Found	Calcd
10	4·70	4·50	5·10	5·82
25	5·09	4·97	5·54	7·38
50	5·44	5·47	7·00	7·80
100	5·75	5·87	7·02	7 90

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[5] W. C. McC. Lewis: "A System of Physical Chemistry," 2nd Ed., 1, 237.

There is unfortunately one complicating condition, the value of the apparent dissociation constant obtained from titration curves is influenced noticeably by the nature of the base used. This is shown by the curves in Fig. 2 which are taken from a recent study made by Baver[6] in the author's laboratory. The curves were obtained by adding increments of the hydroxide solutions to fixed amounts of electrodialyzed Putnam clay. After standing for several days the pH value was measured with the quinhydrone electrode. The usual lyotropic series is quite evident. In the experiments cited above the pK values obtained with KOH were used and K salts were used in the distribution studies. Natural clays contain more exchangeable Ca than any other ion. The calcium pK value would probably more nearly represent natural conditions.

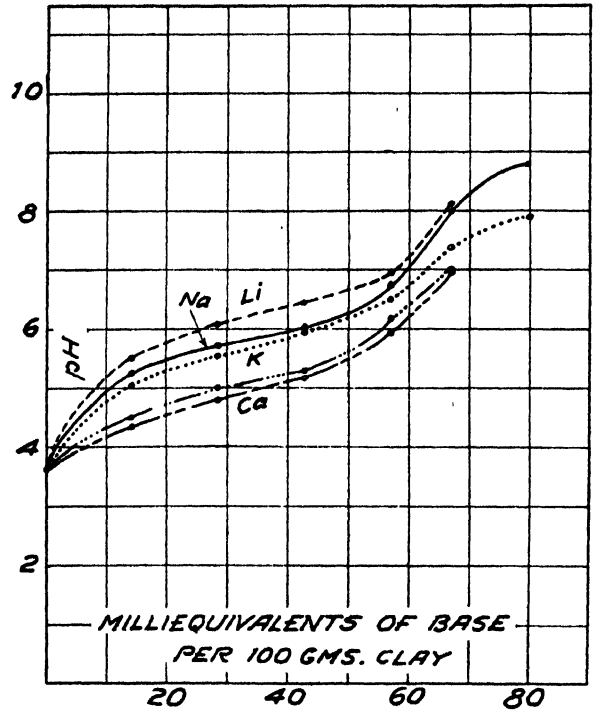

Fig. 2

The change in reaction of clays containing various amounts of different cations. (After Baver).

The Effect of the Amount and Nature of the Exchangeable Cations on the Physical Properties of Colloidal Clays. It has long been known that the physical properties of clays were greatly influenced by the nature of the exchangeable cations. Homoionic clays have usually been prepared in the past by prolonged leaching with a neutral salt of the desired cation. Two objections may be raised against this method: (1) It is difficult to obtain a definite predetermined amount of replacement and (2) it is difficult to remove the last traces of the neutral salt. These objections may be overcome by preparing a stock sol of the hydrogen clay by electrodialysis and then adding the proper amount of the desired cation in the form of the hydroxide. Time does not permit a discussion of all the work that has been done in this field in the last few years but attention will be called to the work of Baver whose results are in general quite typical.

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[6] Missouri Agr. Expt. Sta. Research Bull. 129 (1929).

As changes in the physical properties of clays seem to be correlated usually with changes in electrophoretic potential let us first consider the effect of adding increments of different bases to an electrodialyzed clay (Putnam) on the migration velocity, expressed as v/sec/volt/cm. The measurements were made ultramicroscopically in a cell of the Tuorilla type. The most striking thing in the curves shown in Fig. 3 is the great difference in effects of the monovalent and divalent cations. With the monovalent ions there is a gradual increase to a maximum, then a sharp decline. The maximum comes at the same concentration with each cation and it is identical with the saturation values obtained by conductometric and potentiometric titrations. There is some overlapping of the curves of the monovalent series but in most cases the relationship is what one would expect. The sharp decline in the curves is probably a common ion effect. With the divalent ions a gradual retardation of the velocity is obtained.

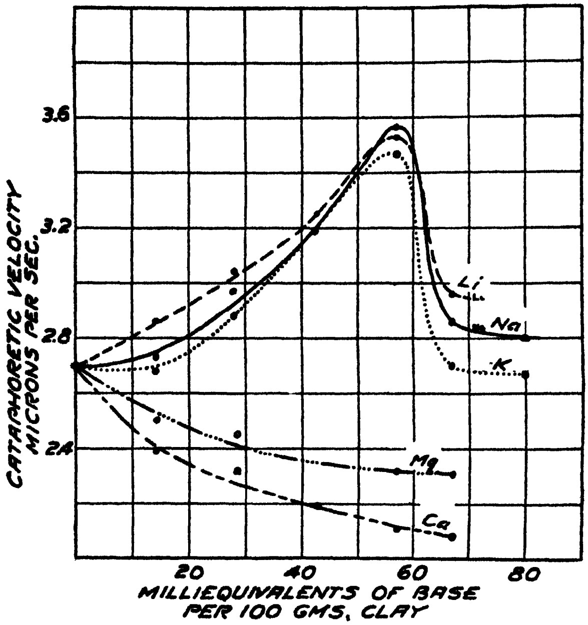

Fig. 3

The migration velocities of clay sols as affected by the amount and nature of exchangeable cations. (After Baver).

There is a marked similarity between the electrophoretic velocities and the viscosities of the sols. The rate of flow of the 2.35 per cent suspensions through the Washburn modification of the Ostwald viscometer is shown in Fig. 4. The relative viscosity of the hydrogen clay was 1.42. For some reason as yet unknown, the maximum of the viscosity curves occurs at a lower concentration of the bases than the maximum of the electrophoresis curves. This may be due to the differences in concentration. It was necessary to use a high dilution, less than 0.01 per cent, in the cataphoresis studies.

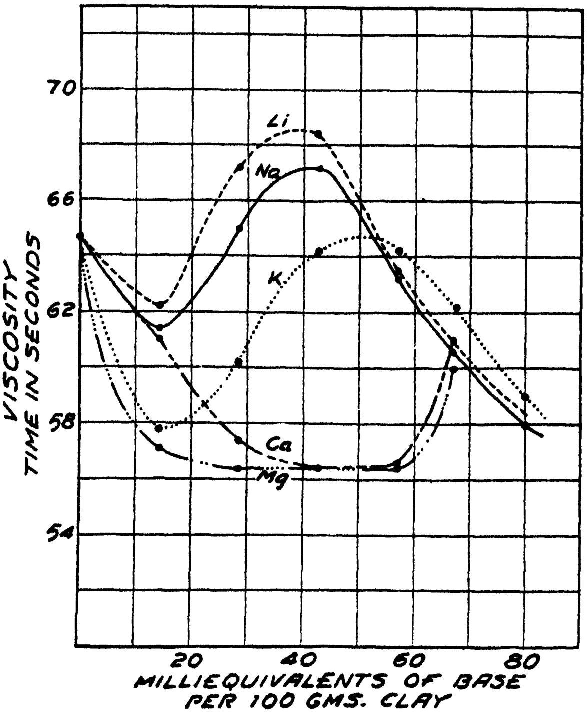

FIG. 4
Viscosity of clay sols containing different amounts of bases. (After Baver).

The initial drop observed with the monovalent cations is due to a dispersion of the aggregates of the hydrogen clay. This effect is most marked in the case of the K sol. The initial increase is undoubtedly associated with the hydration of the cation as pointed out earlier by Wiegner and others. The divalent cations cause a decrease in viscosity up to the saturation point. Further additions cause incipient flocculation. The relative magnitudes of the changes in viscosity caused by the hydration of the particles and by the increase in volume of aggregates due to water entrapped in the micells, can be seen in Fig. 5.

An estimation of the particle-sizes in the clays in the Na and Ca series was made by the ultramicroscopic method. The particles were very large due

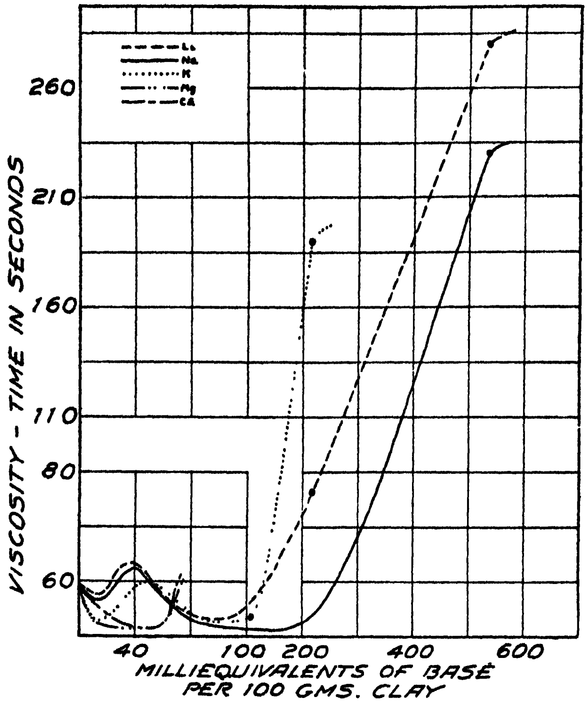

Fig. 5
Viscosity of clay sols containing different amounts of bases. (After Baver).

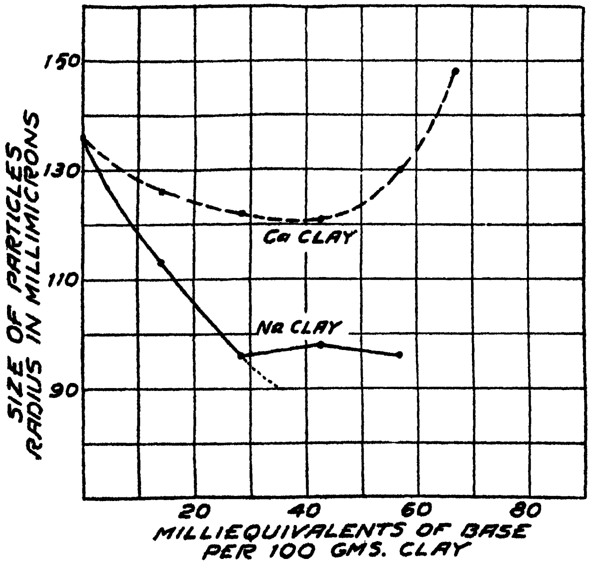

Fig. 6
The effect of exchangeable Ca and Na upon the size of particles of colloidal clay. (After Baver).

in part to the failure to remove all of the particles over 100 μ in the preparation of the clays. Satisfactory counts could be made with the Ca-clay but with the Na-clay it was quite evident that all the particles were not sufficiently visible to permit accurate counts. The shape of the Na-clay curve in Fig. 6 is additional evidence of this. It is not the smooth type to be expected in the light of the other studies.

Another striking illustration of the difference in size between the particles of the Na-clay and the Ca-clay is shown in Fig. 7. These curves represent the velocity of ultra filtration through a collodion membrane under a pressure of 100 pounds per square inch. The Ca-clay is much more permeable. An attempt to calculate the size of the pores in the clay membrane by the formula of Bjerrum and Manegold[7] indicates that the cross section of the pores of the Ca-clay are about eight times as large as those of the Na-clay.

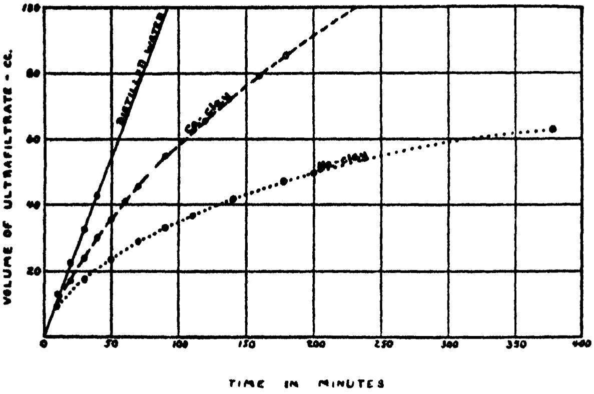

Fig. 7

The effect of exchangeable Ca and Na upon the filtration velocity of clays. (After Baver).

The greater permeability of Ca-clays has long been observed in the field. The unproductiveness of many of our irrigated soils in arid regions has been found to be due to a bad physical condition caused by the replacement of Ca by Na in the colloidal fraction. The formation of clay pans in the humid region, which reduces the productivity of the soils over them to less than 50 per cent of the normal expectation of the region is likewise to be attributed to a replacement of Ca by H. The study of the colloidal behavior of clays is admittedly bristling with difficulties but the results obtained in the last decade seem to justify a continuance of the work in spite of the dire predictions of many prominent colloid chemists, made at the first Colloid Symposium seven years ago.

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[7] Kolloid-Z., 43, 5 (1927).

MEASUREMENTS OF THE PLASTICITY OF CLAYS

BY G. W. SCOTT BLAIR

Introduction

The conception of that property of materials which we call *Plasticity** must have been a fairly important one, even in very early times. This is especially true in the case of clay, where the plastic properties of the material were of so great importance to the craftsman; but although the craftsman was able to judge the quality of his clay with considerable precision, Brongniart[1] was right when he said of plasticity in 1844, "On a souvent parlé de cette propriété, on semble la connaître, mais on n'en a qu'une vague idée." Ever since the time of Brongniart, scientific minds have been trying to define an exact conception of plasticity, and to measure it. An excellent summary of these attempts is to be found in Mellor's Treatise on Inorganic Chemistry, which it is not the purpose of this paper to attempt to reduplicate, but it seems that in spite of all the work that has been done, Brongniart's remark is almost as true today as it was eighty-six years ago.

There can be no doubt that the term "plasticity" has been used by different writers to mean very different things. In some cases the conception may be that of a single physical property, but more often a convenient combination of properties, describing a workable condition of the material, is implied. Without being too dogmatic, we can agree with Mellor to exclude from our conception of plasticity those properties which do not belong to the wet material (in the case of an aqueous two-phase plastic such as clay.) "It is assumed [by certain authors] that the tenacity of the dried clay is proportional to the plasticity of the wet clay. This is generally, but not always true. No known property of the *dry* clay can be used as an infallible index of the plasticity of the *wet* clay," (p. 485). We can scarcely agree that the proportionality is even generally true. Although more circumscribed definitions of plasticity have been suggested (e.g. Karrer[2]) it is thought that the most convenient formula is that of Wilson,[3] which is believed to combine an accurate description of the age-long meaning of the word with a comparatively simple scientific conception. Wilson says "Plasticity is that property which enables a material to be deformed continuously and permanently without rupture, during the application of a force which exceeds the yield value of the material." It is this general conception of plasticity that will be used throughout this paper. It will be seen that such "plasticity" is not *necessarily* related quantitatively either to the binding power of the dried material, as pointed out by Mellor, or to the amount of water which the material will absorb in order to attain its maximum plasticity. The latter property has so often been confused with plasticity, consciously or unconsciously, that many erroneous methods for measuring plasticity have not only been suggested, but have received a fairly wide popularity. This has been particularly true in the case of attempts to relate the plasticity of various colloidal systems to constants derived from curves relating volume of flow to shearing stress, when the material is caused to flow under shear. It seems likely that some such relationship should exist, but previous attempts to define it have invariably resulted in the measurement of a property dependent on the amount of the dispersed phase present, or, where different materials are compared at the same concentration, on the amount of the dispersed phase remaining free; or in other words, on the amount of solvation of the material.

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* Plasticity, from the Latin, plasticus, Greek πλαστικὸς = deformable, mouldable. Plasso (πλάσσω) = I mould.

[1] "Treatise on the Ceramic Arts" (1844). See also J. W. Mellor: "Treatise on Inorganic and Theoretical Chemistry," 6, 485 (1925).

[2] Ind. Eng. Chem., 21, 770 (1929); Anal. Ed., 1, 158 (1929); Rheology, 1, 290 (1930). (This paper contains an interesting discussion on the relation of plasticity to flow-data).

[3] "Ceramics—Clay Technology," 55, etc. (1927).

It seems generally to have been accepted at one time that plasticity is measured by flow data of this type. Bingham,[4] who showed that for many two-phase systems at high rates of shear, the curve relating flow to shearing stress is a straight line which on extrapolation gives an intercept on the stress axis, headed his first discussion on the obtaining of these curves and evaluation of the slope and intercept "The Measurement of Plasticity." Wilson[3] states that the plasticity depends on a combination of both the properties measured by slope and intercept, and that plasticity can be measured comparatively by arranging that the materials are identical with respect to one of these constants, the other then defining the relative plasticity of the materials. (Ref. 3. p. 108.) Bleininger[5] is rather less definite, speaking of "plastic properties" rather than "plasticity" itself.

It is the object of the present paper to discuss the relationship between flow-stress curves and the plasticity of aqueous clay pastes, and then to consider how flow curve data can be used to investigate the causes and control of the plasticity of such clay pastes.

Some Empirical Plasticity Tests

In order to compare flow constants with the plasticity of a clay, it is necessary to have some simple tests of plasticity depending fairly strictly on the definition, or accepted by the experts as giving on the whole a good rough measure of plasticity, as a standard of comparison. The author has developed a test for this purpose which will be described first, as it seems the most satisfactory of those used.

Atterberg[6] has described a test in which a plastic mass of clay in water is rolled out into a fine "wire," the moisture content at which the wire or thread just tends to crumble being recorded. This is called the "Lower Plasticity Limit" of the clay, and gives a measure of its hydration capacity. To measure plasticity roughly, this test has been modified in the following way. A small pellet of plastic clay is rolled into a thread or wire very carefully with the finger, on a piece of smooth paper. This is done at that water content which gives the thinnest possible thread before crumbling takes place. The determination of the right moisture content is done by trial and error in the hands, and with a little practise becomes fairly easy. The moisture content need not be measured, but the diameter of the thinnest "wire" of clay that can be rolled is measured with a gauge. This test is believed to give a good rough indication of the extent to which the most plastic mass which can be made from the clay can be "deformed without rupture", and appears to correlate well with other information about the plasticity of clays. For convenience this will be referred to as "The Wire Test".

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[4] "Fluidity and Plasticity," 320 (1922).

[5] J. Ind. Eng. Chem., **121**, 436 I1920).

[6] Internat. Reports on Pedology (1911) etc. See also Kinnison: U. S. Bur. Standards, Tech. Papers, No. 46 (1925); Wilson: Ref. 3, p. 114.

Two other empirical tests have been used which give some measure of the plastic properties of a clay. The first, called "The Slaking Test", has been used a good deal by practical ceramists. (It has also been called "The Bancroft Test.")[7] In this test, a mass of clay is kneaded under the thumb into a ball at what is termed the concentration of maximum plasticity, (though actually this is rather drier than the concentration of maximum plasticity as used for the wire test), allowed to dry out at room temperature over night, and then placed in distilled water in such a way that the material which falls away as the water replaces the cementing material in the ball, is able to fall clear of the mass of the clay. The time taken for a ball made from a given weight of clay to disintegrate completely is termed the "Slaking-Time", and it has been claimed that this gives a good measure of the plasticity of the clay.

In view of what has been said earlier in this paper, it is not surprising that although in many cases this test measures something so near to plasticity as to make it highly useful, experiment shows that in certain cases the slaking-time does not depend directly on plasticity at all, but rather on other properties of the material.*

The second, the "Oil Filtration Test", depends on the phenomenon investigated by Nutting,[8] who claims that the extent to which a clay is able to remove coloured impurities from a heavy oil by filtration, depends on the presence of hydroxyl groups, and open bonds in the clay. Dr. Nutting suggested to the writer of this paper that this property might be related to the plasticity of clay, and although the method is quite indirect, and although the author has not been able to obtain such regular and reproducible results as has Nutting, yet there does appear to be a very close correlation between the oil filtration capacity of a clay and its plasticity. Since work on this test is still in an early stage, no detailed technique will be described.

Having described a few rough tests by which some idea of the relative plasticity of a batch of clays may be obtained, we can now proceed to give an account of the way in which flow-constants are obtained. The modified Bingham plastometer used in this work has already been described.[9] A paste of the clay is caused to flow between two pipette bulbs through a glass capillary tube of known dimensions at a series of different pressures, the volume of material flowing through the capillary at each pressure being determined by means of a flowmeter somewhat similar to that described by Green.[10] The shape of the flow curve thus obtained has been much discussed, both from the theoretical and experimental points of view (for references see (9)), but in general, the following is a brief outline of its character.

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[7] Bancroft and Jenks: J. Phys. Chem., **29**, 1215 (1925); Jenks: **33**, 1733 (1929); Boyd: J. Am. Soc. Test. Mat., **22**, 337 (1922); Middleton: U. S. Dept. Agri. Tech. Bull., No. 178 (1929).

* Bancroft and Jenks are quite clear on this point.

[8] J. Washington Acad. Sci., **18**, 409 (1928). See also Haseman: J. Phys. Chem., **33**, 1514 (1929).

Up to a certain small, but quite definite pressure (a), there is no flow at all (Fig. 1. stage I.); then follows a stage (II) in which the material flows as a solid plug through the tube, the flow-curve being rectilinear. This plug may be regarded as sliding through a water-envelope of constant thickness. The intercept (a) may be regarded as the shearing-strength or yield value of this water-envelope, or as a measure of the adhesion of the plug to the wall of the tube. It appears that these water films show rigid properties up to a thickness of at least 10^{-4} cm. (minimum value).* When another critical pressure (b) is reached, the curve slopes sharply upwards, and streamlining takes place near the wall of the tube (stage III.), the material still moving as a plug in the centre. As pressure is still further increased this plug diminishes at the expense of the streamlining sheath surrounding it, until finally almost the whole of the material is streamlining, the flow curve being again rectilinear (stage IV.). The extrapolated intercept (c) of this last straight line to the pressure axis gives Bingham's "yield value",[4] or as we prefer to call it, the shearing strength of the material.

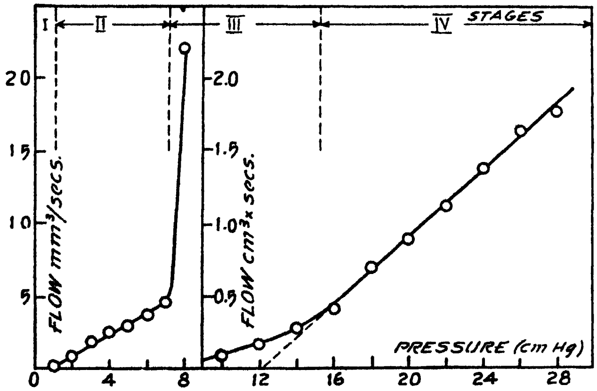

FIG. 1

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[9] G. W. Scott Blair: Rheology, 1, 127 (1930); G. W. Scott Blair and E. W. Crowther: J. Phys. Chem., 33, 321 (1929); G. W. Scott Blair: J. Phys. Chem., 34, 1505 (1930); R. K. Schofield and G. W. Scott Blair: 34, 248 (1930); B. A. Keen and G. W. Scott Blair: J. Agric. Sci., 19, 648 (1929).

[10] J. Am. Soc. Test. Mat., 20, 450 (1920). A detailed description of the apparatus and technique are given in the paper by Keen and Crowther, listed under Ref. 9.

* This is calculated on the assumption that at concentrations where the water-film is only just thin enough to show rigid properties, its viscosity is of the same order as that of ordinary water. Compare Weber and Lewin: Kolloid-Z., 50, 197 (1930).

Experimental

A preliminary attempt was made to correlate mobility (slope of stage IV of curve) and the shearing strength of five clays with the order of their plasticity as determined by the rough tests described above, and alternatively with their water-absorbing capacity (moisture content at maximum plasticity). It will be apparent from Table I that these plastic constants depend on the water-absorption capacity rather than the plasticity. The clays were compared in the plastometer at a constant concentration by weight.

TABLE I

Clay	Slaking time mins. (2.5g.)	Wire test diameter mm.	%^{ge} dry matter at condition of maximum plasticity.	Shearing strength (c) (pressure) cm. Hg.	Mobility
1	3.6	2.0	71.0	12.5	0.95
2	4.3	1.0	79.5	0.3	2.5
3	18.5	0.6	77.0	1.6	1.3
4	> 50.	<0.6	72.5	3.3	1.25
5	9.0	0.8	75.0	3.3	1.1

Order of oil filtration capacities:—$1 < 2 < 5 < 3 < 4$.

An attempt to compare mobility and shearing strength of clay pastes made up to equivalent concentrations in free water by allowing for water absorption capacity differences was unsuccessful. It is also found that the slope and intercept of the "plug"-curve (stage II) depend on hydration rather than plasticity, when comparisons are made at the same concentrations either by weight or volume.

A Relationship between Plasticity and the Flow Curve

After a very careful study of all the data available, it was found empirically that *when clays are compared at concentrations such that their a-values (adhesions to the wall of the tube) are the same, in tubes made of the same kind of glass, then under these conditions, the shearing strengths of the materials give a good measure of the relative plasticity of the clays.*

TABLE II

Clay*	B_A	Diam. of "wire" mm.	Clay*	B_A	Diam. of "wire" mm.
A	2.82	0.6	H	1.64(?)	2.1
B	2.66	0.6	I	1.59	1.8
C	2.36	0.7	K	1.59	2.0
D	2.21	0.8	L	1.58	2.5
E	2.05	1.1	M	1.38	3.0
F	1.85	1.0	N	0.82	5.0
G	1.69	2.0—	O	0.56	9.0

B_A is the value of B, when $aR/2L$ is 0.21 dyne/mm^2

* These materials are not all strictly "clays."

Table II shows the relationship between B, the critical shearing stress per unit area at the wall, (which is bR/2L, where R is the radius of the tube and L its strength), to the diameter of "wire" from the wire test. A fairly good correlation for a large number of materials is shown.

In these cases, the concentration which would give the arbitrarily fixed value of "a" was first determined for each material by trial and error, but when it was observed that for different concentrations of the same material, a and b were at any rate roughly linearly related, it was found much simpler first to do a test at a value of "a" slightly higher than is required, and then to dilute to a slightly lower value, calculating the value of b for the intermediate arbitrary "a" value by means of an interpolation formula. The a/b curves do not pass through the origin, and the question arises as to whether plasticity determined in this way is really independent of the arbitrary value of "a" chosen. Actually the relative values are not quite independent of "a", if the clays are compared at very widely different "a" values. Plasticity probably depends in some complex way on the entire a/b curve; but for practical purposes, the simple test, taking a suitable value of "a", is considered as giving a fairly reliable figure, though a complete and much more complicated test could easily be devised if greater accuracy were required. For ordinary purposes, a flow curve derived from a single capillary is adequate, but it is best to define the constants as stresses per unit area at the wall, in this way making the values independent of the dimensions of the tube.* It has been found (9) that there is a modification in the flow properties of clay pastes in the immediate vicinity of the wall of the tube. This means that B is not really a true measure of the critical shearing stress of the whole bulk of the material. However, at high concentrations this effect is small, and the correction not serious; for this reason the arbitrary "A" value should be taken as high as is convenient. If a slightly less simple test is no disadvantage, the extrapolated intercepts of the stage IV part of the curve can be taken instead of B. We will then define *the critical shearing stress at the wall in a paste of a clay having an adhesion at the wall equal to one dyne per square millimeter as the Flow-plasticity* (B_{A1}). One dyne/mm^2 is quite a convenient value for "A" for the less plastic clays. For very plastic clays, a lower value may be used (as in Table II). The word "Flow-plasticity" is used in order not to be too dogmatic about the exact nature of plasticity. Flow-plasticity is at least something very much like the Wilson definition of plasticity, and can be measured quickly, easily and with fair accuracy.

The Mechanism of the Test

It is not understood exactly why plasticity can be measured in the way described. It is not surprising that the critical shearing stress of the material should be related to plasticity, but why it should be necessary to compare clays at the same wall-adhesion is not at all clear. One must remember that the idea of a water envelope surrounding the plug is conventional, each particle of clay being hydrated. The hydration layers round the particles may be distorted at the wall, but in any case the thickness of the water envelope refers simply to the mean distance between the outermost particles forming the moving plug, and the wall of the tube. The clays are compared at such concentrations that the shearing strength of this thick layer of water molecules is the same in all cases. That this procedure should give results which yield comparable plasticity figures for different clays is a fact which must at present be regarded as empirical, but it is hoped that some explanation will shortly be forthcoming.

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* If the force per unit area of the cross-section of the capillary is p, the total force, $p\pi R^2$, must be equal to the total stress on the wall of the capillary. Since the area of the wall is given by $2\pi RL$, the stress per unit area on the wall is given by pR/2L. Throughout this paper, pressures are written with small letters, and stresses per unit area with capitals. Thus A = aR/2L, and B = bR/2L.

The Performance of the Test

The following is an account of the exact way in which the test is carried out. Clay is mixed with distilled water into a thick paste,* forced through a 100-mesh-per-inch sieve, diluted to a concentration slightly greater than that required, (with a little practice this is quite easily done,) then placed in the plastometer in the thermostat. The paste is first forced rapidly through the capillary to eliminate thixotropic structure, and ensure good mixing, and is then forced backwards and forwards by compressed air as previously described[9] at a series of pressures ranging from zero to a point where streamline flow has begun. The flow curve is then plotted (a typical curve is given in Fig. 2), and A and B are calculated. These we will call A_2 and B_2.

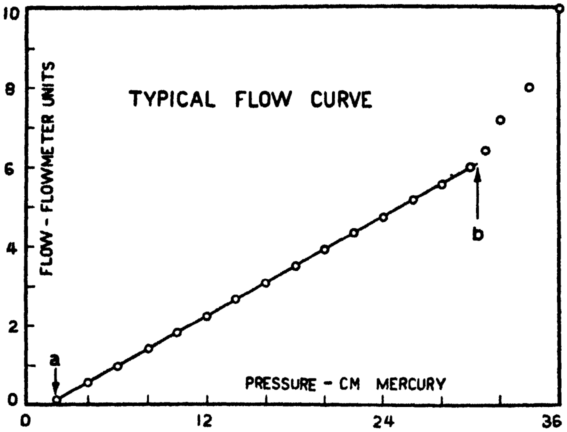

Fig. 2

The paste is then removed from the plastometer, diluted slightly, mixed thoroughly, and the test is repeated, the constants A_1 and B_1 being evaluated. The arbitrary A value, (normally 1 dyne/mm^2.), should lie between A_2 and A_1. Then we have;—

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* It is sometimes necessary to work the material for some time before a really smooth paste is obtained.

$$B_{A1} = \frac{(B_2-B_1)\ (1-A_1)}{(A_2-A_1)} + B_1$$

an equation which assumes only that A and B are linearly related over a small range of concentration—which is certainly true. Should there be any doubt as to the accuracy of a test, a third concentration, or even a different capillary may be used. The whole test normally takes rather less than one hour to complete. Attempts to use a simpler type of plastometer for this test, (the Bingham-Murray for example,)[11] have not proved encouraging so far.

The Causes and Control of Clay Plasticity

Having developed a test for measuring the plasticity of clay, it is of interest to find out how far the use of this new test substantiates or refutes earlier theories on the ways in which plasticity may be produced or increased in a clay. Bancroft and Jenks[7] have suggested that a clay may be rendered more plastic by treating it with a flocculant in the presence of a peptizing medium, and have shown that this is actually the case, if the slaking test is taken as a measure of plasticity. Table III shows the effect of treating a kaolin sample with (1) NaOH (2) NaCl (3) NaOH + NaCl, the material being boiled on a water-bath to dryness for about four hours, and then once more made into a paste, and tested by the flow-plasticity test. It is clear that the combined action of the NaOH and NaCl has a very marked plasticizing effect.

The use of solutions of potassium tartrate and sodium citrate as peptizing media give a similar, but less marked effect.

TABLE III

Treatment	B_{A1}	%ge increase B_{A1} on control
Control	6.4	——
1% NaOH	2.15	−66
5% NaCl	7.4	+16
1% NaOH + 5% NaCl	10.2	+59
5% Potassium Tartrate	6.1	− 5
5% Potassium Tartrate + 5% NaCl	8.5	+33
5% Potassium Tartrate + 5% KCl	8.0	+25
5% Sodium Citrate	7.2	+12.5
5% Sodium Citrate + 5% NaCl	8.7	+36

(All concentrations are given as percentages of dry clay.)

However, kaolin can be rendered more plastic in a number of other ways as well as by the action of a flocculant in the presence of a peptizing medium. The mechanism of the processes is not quite clear, but if kaolin is treated with increasing quantities of HCl, the plasticity is increased up to an optimum concentration, after which it falls again. Sulphuric acid, or mixtures of sulphuric acid and aluminium sulphate plasticize kaolin to an enormous extent. The results of these preliminary experiments are given in Table IV.

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[11] J. Am. Soc. Test. Mat., **23**, 655 (1923).

TABLE IV

Treatment	B_{AI}	$\%^{ge}$ increase B_{AI} on control
Control	6.4	——
0.18% HCl	8.3	+ 30
0.37———	11.0	+ 72
0.44———	14.2	+122
0.55———	10.4	+ 63
1.1 ———	6.4	0
0.73% H_2SO_4	17.0	+166
0.73% HS_2O_4 + 2% $Al_2(SO_4)_3$	21.9	+242

Experiments on the effect of mixed electrolytes are in progress. It is of interest to note that whereas the slaking test shows an increased plasticity on the addition of NaOH to clay alone, both the flow-plasticity test, and the wire test show a decrease. This is much more in accordance with general experience. These investigations are still in a preliminary stage, and are being continued.

Summary

The meaning of the term plasticity is discussed, and various simple, rough tests for the plasticity of a clay are described. It is shown that when different clays are caused to flow through a capillary tube under stress at the same concentrations, the ordinary flow constants, mobility and shearing strength (or yield value) depend on the hydration capacity of the clay rather than on its plasticity. By comparing the flow of clay pastes at such low shearing stresses that the material flows as a solid plug, and arranging the concentrations so that the water envelope surrounding the plug has a constant shearing strength, it is possible to get values for the critical shearing stress of the material, which depend on a property very closely allied to plasticity, to which the term "Flow-plasticity" has been applied. Preliminary work on the effect of electrolytes on the flow-plasticity of kaolin is described, with special reference to the Bancroft-Jenks theory of mixed peptizing and flocculating action.

The author is much endebted to Professor Wilder D. Bancroft for his constant help and advice throughout the progress of this work, and to the Norton Company of Worcester (Mass.) for their kindness in supplying some of the clays used.

Cornell University.

STUDIES IN THE PLASTICITY OF PAINTS

BY F. H. RHODES AND W. J. JEBENS[1]

The plasticity of paints has been extensively studied in connection with their brushing characteristics. Among the various factors that affect the plasticity, the following are some of the more important ones—the volume concentration of pigment, the size and shape of particles, the extent to which the pigment is wetted by the vehicle, the extent to which the pigment is flocculated in the paint, the viscosity of the vehicle, the presence of soap, the presence of water, and the age of the paint. As the concentration of the pigment in the paint is increased, the mobility of the material is decreased and yield value is increased. Rhodes and Wells[2] found this to be true with paints made with the following pigments: zinc oxide, lithopone, Dutch process white lead, basic sulphate white lead, electrolytic white lead, and titanox. Although theoretically the yield value is zero for values of concentration lower than that required for cubical packing of the pigment particles, a small yield value is obtained experimentally. The mobility of the suspension decreases linearly with the concentration of the pigment in the paint.[3,4]

For particles of fairly uniform size and shape the yield value increases and the mobility decreases with a decrease in the average diameter of the particles. Einstein[5] in deriving his formula for the viscosities of dilute suspensions neglected the effect of the size of the particles as modified by adsorption. Hatschek[6] called attention to the error introduced by this omission. However for paints prepared from zinc oxide and linseed oil, Green and Haslam[7] have shown that the yield value increases as the particle size decreased. Odén[8] found an increase in the viscosity for sulphur sols with increased dispersion of the sulphur, the effect being more pronounced the higher the concentration of the sulphur. It has also been noted that the form of the size distribution curve for the pigment affects the plastic characteristics of the paint.[9]

A third factor that may affect the plastic characteristics of a paint is the ease with which the solid is wetted by the liquid. Both the nature of the pigment and the nature of the vehicle affect the ease of wetting. In general, an increase in the ease of wetting causes an increase in the mobility and a decrease in the yield value. In some instances, the wettability of the pigment varies greatly with apparently minor changes in the composition of the vehicle.

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[1] DuPont Fellow in Chemistry at Cornell University.

[2] Ind. Eng. Chem., **21**, 1273 (1929).

[3] Bingham, Bruce, and Wolbach: J. Franklin Inst., **195**, 303 (1923).

[4] Bingham and Jacques: Ind. Eng. Chem., **15**, 1033 (1923).

[5] Ann. Physik, (4) **34**, 591 (1911).

[6] Kolloid-Z., **1**, 301 (1910).

[7] Ind. Eng. Chem., **19**, 53 (1927).

[8] Z. physik. Chem., **80**, 709 (1912).

[9] Ingalls: Am. Paint Var. Mfg. Assocn. Circ. 135.

For instance, a small increase in the concentration of free fatty acids may cause the oil to wet the pigment much more readily. It is well known that linseed oil will displace water from pulp-mixed white lead only if the acid value of the oil is above a certain minimum limit.[10]

The extent to which the pigment in the paint is flocculated depends upon the nature of the pigment and upon the character of the vehicle. In general, the deflocculation of the pigment is more nearly complete when the solid is readily wetted by the liquid. In some cases, the effect of the degree of flocculation upon the consistency of the suspension is very pronounced. The effect of the addition of a deflocculating agent upon the plastic characteristics of a suspension may be illustrated by adding a small amount of oleic acid to a mixture of lithopone and mineral oil. If dry lithopone is mixed with a considerable amount of mineral oil, the pigment remains in a highly flocculated condition, and the resulting mixture is a stiff paste which can be shaped and moulded like clay. If a few drops of a deflocculating agent—as, for example, oleic acid—are added, the lithopone is wetted and dispersed, and a mobile suspension results. The addition of the dispersing agent greatly increases the mobility but decreases the yield point only slightly. The flocculating power of a liquid is one of the important factors in determining its characteristics as a thinner for paints. All of the commonly used thinners—benzol, petroleum naphtha, and turpentine—have viscosities of the same general order of magnitude. Turpentine, however, tends to flocculate certain pigments, and therefore in reducing the paint to the desired consistency it is necessary to add more of the turpentine than of any of the other thinners.[2,11]

A decrease in the viscosity of the medium increases the mobility of the suspension but has little or no effect upon the yield point. In many cases the effect of the viscosity of the liquid is small in comparison with that due to its wetting power.

The addition of soaps to a paint results in "false" body. Bingham and Jacques[4] found that the addition of aluminum stearate to a paint made with lithopone and linseed oil increased the yield value markedly, but lowered the mobility only slightly. The effect of soaps in lubricating greases is much better known than their effect in paints, and it may be of interest to give some of the facts concerning them. The structure of a soap in a lubricating oil is probably much the same as that given by McBain for water solutions of soap.[12] If the soap is quite soluble in the oil there is little increase in the consistency of the grease. This is true with greases made with calcium oleate where in order to obtain proper consistency it is necessary that water should be incorporated in the solution of soap in oil. Sodium soaps incorporated in a grease are practically completely dehydrated and are able to give a very stable structure in this state. Lead soaps are very much less soluble in the oil and tend to precipitate out if too much water is present. Zinc soaps are never used alone in the manufacture of greases as they have little ability to thicken the oil and are very unstable in the presence of moisture. The effect due to soaps in paints if similar to their effect in greases will vary widely depending on the type of soap and the conditions.

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[10] Smith: "The Manufacture of Paints" (1915).

[11] Wolff: Chem.-Ztg., **48**, 647 (1924).

[12] Kleingard: "Lubricating Greases" (1927).

Bingham and Jacques[4] found that the addition of small amounts of water to a paint made with dry lithopone and linseed oil increases the yield value and decreases the mobility. It does not follow, however that the presence of water always injures the brushing qualities of a paint; in fact, it is common experience that in many cases paints which contain small amounts of water "brush out" much better than do those made from absolutely dry materials.[13] The superior working qualities which are claimed for pulp-mixed white lead may be due in part to the fact that this material always contains a small amount of moisture.[14]

In many instances, ready mixed paints tend to undergo changes in texture and plasticity on standing. The oil may hydrolyze to some extent, and the free acids thus formed may react with the pigment to form soaps.[15] In certain cases, the formation of these soaps may tend to cause "skinning" and "puttying." Furthermore, the slow reactions that occur during ageing may change, and in some instances may improve, the plastic characteristics. Sabin[16] states that "The fluidity and working characteristics of white zinc paint are considerably improved with age." Bingham and Jacques[4] found that with continued grinding the yield value at first decreases and then remains constant, while the mobility at first rises and later decreases. The effects may be due in part to changes which are analogous to those which occur during ageing.

Experimental Procedure

The linseed oil used in preparing the paints was pure refined linseed oil from North American seed. The two lots of oil which were used were analyzed by the methods recommended by the A. C. S. Committee on Analysis of Commercial Fats and Oils with the following results:

	Lot 1	Lot 2
Acid number	0.459	0.280
Saponification number	189.800	194.500
Iodine number	194.300	182.700
Specific gravity	0.9275	0.9276

The pigments were zinc oxide, Dutch process white lead, aluminum powder, and iron oxide.

In the preparation of the paints, the following procedure was adopted: The required amount of pigment was weighed into a mortar, and sufficient linseed oil was added to form a thick paste. The mixture was ground for thirty minutes. The remainder of the oil required to give a paint of the desired composition was then added slowly and with constant grinding, and the grinding was continued until the pigment was thoroughly incorporated in the vehicle and a homogeneous paint was obtained. The paint was passed through a 200-mesh sieve and was then placed under a vacuum for several hours and stirred at intervals to eliminate bubbles of air.

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[13] Toch: "Chemistry and Technology of Paints" (1925).

[14] Sabin: "White Lead: Its Uses in Paints" (1920).

[15] Ware and Christman: Ind. Eng. Chem., 8, 897 (1916).

[16] "Technology of Paints and Varnishes" (1917).

Paints free from moisture were prepared from dry linseed oil and pigment which had been dried for two hours at 120°C. In the preparation of the paints which contained water, the required amount of water was weighed into a mortar and a portion of the dry paint was added. The mixture was ground until homogeneous, then the rest of the dry paint was added with constant grinding and the grinding was continued until thorough incorporation of the water was attained. To remove any air which may have been introduced during this operation, the wet paint was again evacuated for thirty minutes with almost constant stirring. Some of the water in the paint was vaporized during the second evacuation. The water content could not therefore be calculated from the proportions used in preparing the paint and was determined by analysis.

The same apparatus and procedure was used to measure the plasticity of the paints as was used by Rhodes and Wells.[2] The capillary used in this work was 6.05 cm long and 0.0247 cm in radius. The pressures were measured in centimeters of mercury, and are so expressed in all of the following tables. With the particular capillary which was used, a pressure of one centimeter of mercury is equivalent to a stress of 27.06 dynes per square centimeter. All yield points, as given, may be converted to the absolute basis by multiplying by this factor. The mobilities, as given, are expressed in terms of the slopes of the graphs obtained by plotting rates of flow, in cubic centimeters per minute, against the corresponding pressures in centimeters of mercury. While these units are perfectly satisfactory for purposes of comparison, they may be converted into absolute units by multiplying by the factor, $8L/R^4Dg$, in which, L is the length of the capillary in centimeters, R is the radius of the capillary in centimeters, D is the density of mercury (13.596), and g is the gravity constant (980.4). The numerical value of this constant, for the capillary used, was 52.03.

Experimental Results

Effect of Water. Paints were prepared from dry neutral linseed oil (Lot 1) and each of the following pigments: zinc oxide, white lead, mixtures of white lead and zinc oxide, and iron oxide. To each of the dry paints, various amounts of water were added, and the plasticities of the resulting paints were determined. The results are summarized in Table I.

The addition of water to paints made with oil of low acid value increases the yield and lowers the mobility—*i.e.*, it renders the paint considerably stiffer and less fluid. In general, the effect of the addition of water upon the mobility appears to vary qualitatively with the relative ease with which the

TABLE I

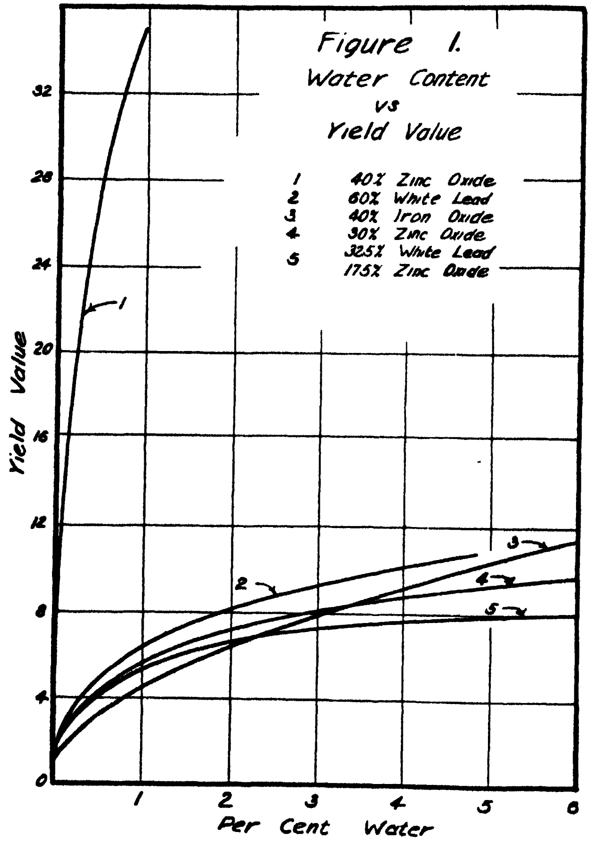
Effect of Water on Paints prepared from Neutral Linseed Oil

Pigment	% by weight of Pigment	Water Content	Yield Value	Mobility
Zinc Oxide	30%	0.00%	1.5	0.0306
		0.40	4.3	0.0190
		0.89	5.4	0.0190
		1.84	6.9	0.0168
		4.75	8.2	0.0168
		7.77	10.0	0.0147
Zinc Oxide	40	0.00	4.9	0.0240
		0.99	35.2	0.0147
White Lead	60	0.00	1.0	0.0226
		0.42	4.5	0.0139
		0.76	6.0	0.0127
		1.83	7.0	0.0116
		4.87	10.8	0.0089
Mixture:	50	0.00	1.5	0.0272
65% white lead		0.50	4.3	0.0138
35% zinc oxide		1.02	5.5	0.0126
		1.86	6.7	0.0120
		4.92	7.8	0.0110
		7.78	10.2	0.0114
Iron oxide	40	0.00	1.0	0.0221
		0.44	2.1	0.0212
		0.96	5.0	0.0196
		1.79	6.2	0.0188
		4.54	9.8	0.0160
		7.38	12.2	0.0126

The results are shown graphically in Figs. 1 and 2.

pigment is wetted by water. In the paints made with white lead, which is very much less readily wetted by water than by oil, the first small additions of water very greatly decrease the mobility; with larger amounts of water the effect is still apparent, although much less pronounced. Somewhat similar results were obtained with the paints made with mixtures of white lead and zinc oxide. Paints containing zinc oxide alone, which is somewhat more readily wetted by water than is white lead, also showed a rather marked decrease in mobility with the first additions of water, but the effect was somewhat less pronounced. With iron oxide, which is rather readily wetted by water, the decrease in mobility was less pronounced and was more nearly linear throughout the entire range of concentrations.

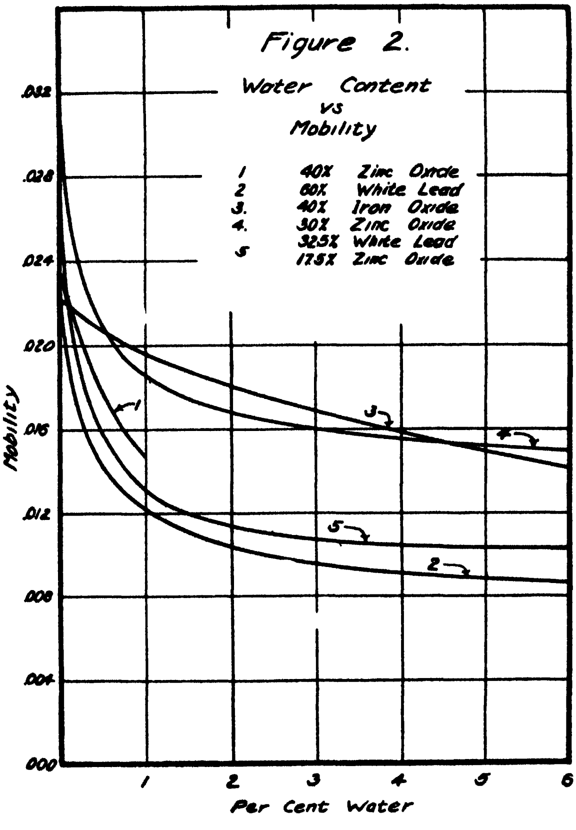
With each of the paints, the first small additions of water increased the yield values markedly, further increase in the content of water had relatively less effect. All of the dry paints except that one which contained forty per cent of zinc oxide had yield values of the same general order of magnitude, and with all of these paints the effect of the addition of water was quite similar. The initially high yield value of the paint which contained forty per cent of zinc oxide was increased very rapidly indeed by the addition of small amounts of water, so that at first glance it would seem that the effect of water upon the plasticity of this paint is unusually great. It will be observed, however, that the proportional increase in yield value which is brought about by the addition of water to the dry paint is approximately the same with all of the paints.



The increase in the consistency of all these paints is probably due to the action of the water in tending to flocculate the pigment and to form an emulsion of water in the paint. In either case a structure is built up in the paint with the resulting increase in yield value and decrease in mobility.

The Effect of Soaps. The effect of the addition of soap upon the plastic characteristics of paints was studied for the two soaps, sodium oleate and calcium oleate. These particular ones were selected because they are typical of the two principal classes of soaps: sodium oleate is soluble in water and tends to aid in the formation of emulsions of oil in water, while calcium oleate is soluble in oil, and tends to produce emulsions of water in oil.

In preparing these paints, an amount of soap equal to ten per cent of the weight of the combined oil and pigment was placed in a mortar, and to it was added a small amount of the linseed oil. After grinding the soap and the oil together thoroughly, the pigment and the remainder of the oil were added and the paint prepared in the usual way. All of the paints contained thirty parts by weight of zinc oxide to seventy parts of linseed oil (Lot 2). Mixtures containing less than ten per cent of soap were made up by blending portions of this paint with the proper quantities of paint which contained no soap. The results of the plasticity determination are given in Table II and are shown graphically in Figs. 3 and 4.



These results are qualitatively significant, but may not be extremely accurate quantitatively. The soaps—and particularly the sodium oleate—probably exist in the paint in the form of micelles or minute threads which give the mass a "false body". The mere stirring of the solution, or the dis-

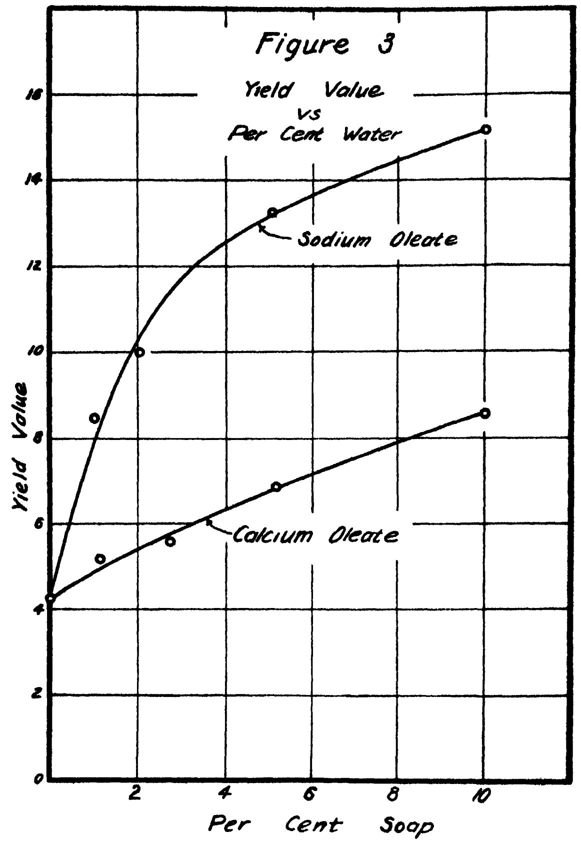
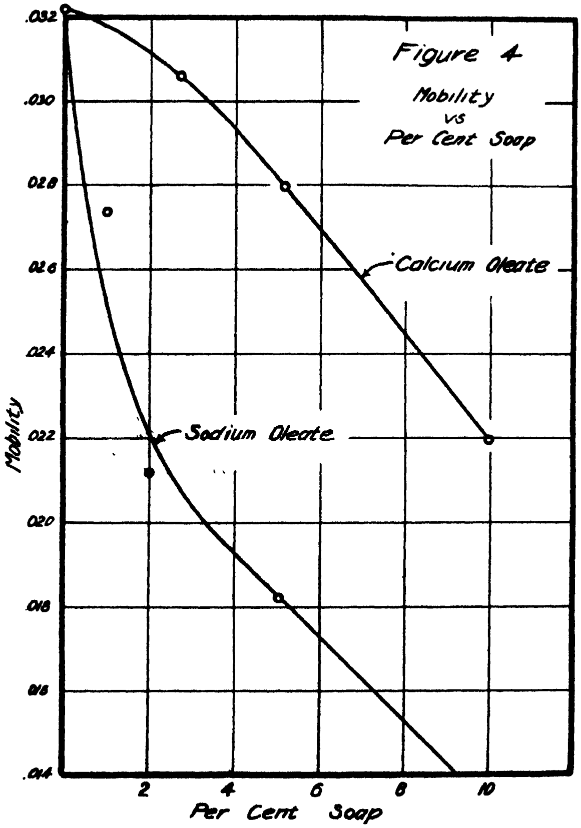


Table II

Effect of Soaps on Paints prepared from Neutral Linseed Oil

Soap	Per Cent of Soap	Yield Value	Mobility
Calcium Oleate	0.00	4.3	0.0322
	1.18	5.2	0.0318
	2.72	5.6	0.0306
	5.19	6.9	0.0280
	10.00	8.5	0.0220
Sodium Oleate	0.00	4.3	0.0322
	1.02	8.5	0.0274
	2.01	10.0	0.0212
	5.10	13.3	0.0182
	10.00	15.2	0.0132

tortion which occurs when the mass flows through the outlet tube of the plastometer, may disrupt this structure to some extent, and may therefore cause a change in plasticity during the determination. It is well known that a change in the plasticity of a lubricating grease—a suspension of soap in mineral oil—does occur when the grease is passed through a capillary tube, and it is to be expected that a similar change will occur with a suspension of a soap in a vegetable oil.



The addition of either sodium oleate or calcium oleate increases the yield point and decreases the mobility of the paint, but the effects are much more pronounced in the case of the sodium soap. This is to be expected. The calcium oleate is quite soluble in the soil, and probably exists either in true solution or in a highly dispersed condition, while the sodium oleate is much less soluble in linseed oil, and probably exists principally in the form of thread-like micelles.

Joint Effect of Soap and Water. Various amounts of water were added to paints which were made up with 30 parts of zinc oxide, 70 of linseed oil and 2 of soap. The results are shown in Table III and Figs. 5 and 6.

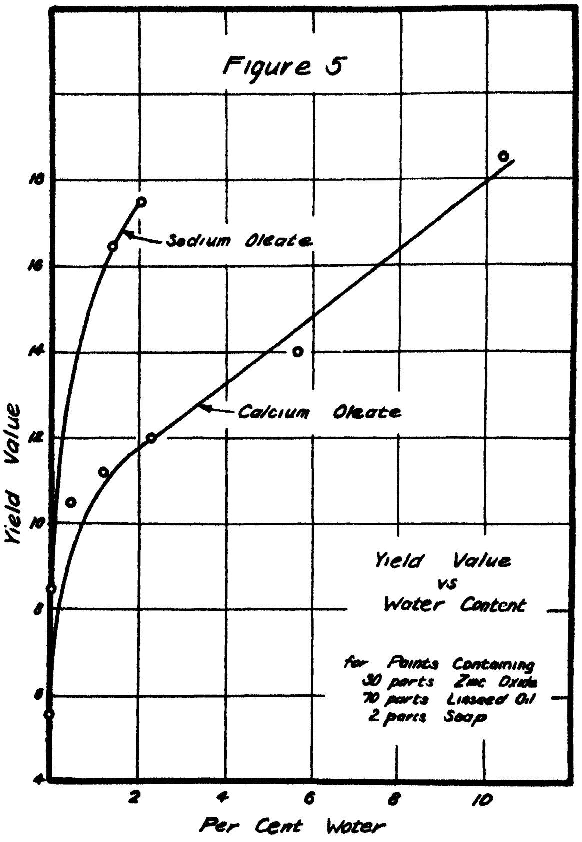
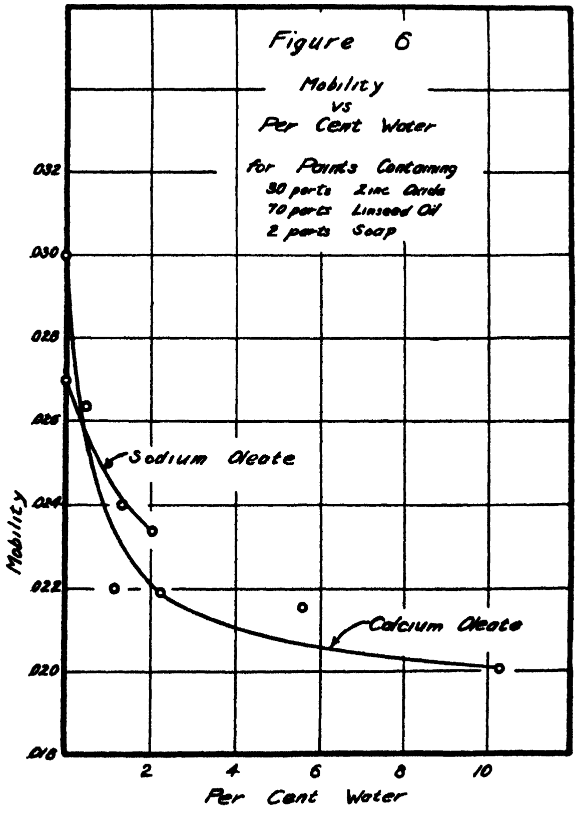


Table III

Joint Effect of Soap and Water on Paints prepared from Neutral Linseed Oil

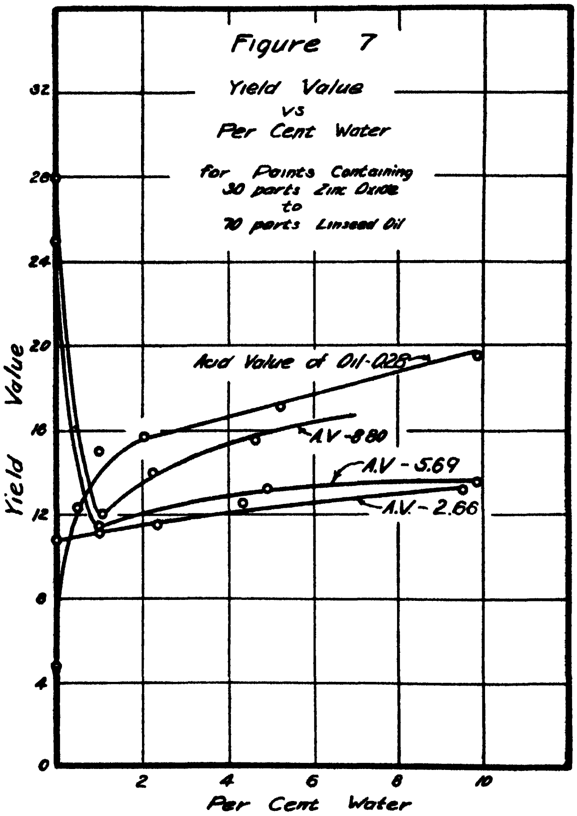
Soap	Per Cent of Water	Yield Value	Mobility
Calcium Oleate	0.00	5.5	0.0300
	1.19	11.2	0.0220
	2.25	12.0	0.0219
	5.62	14.0	0.0216
	10.31	18.5	0.0200
Sodium Oleate	0.00	8.5	0.0270
	0.48	10.5	0.0264
	1.36	16.5	0.0240
	2.05	17.5	0.0234

With the paints containing sodium oleate, difficulty was experienced in obtaining complete and permanent emulsification when the water content was over two per cent. A very thick mixture was obtained when the water was first emulsified but in a few minutes the zinc oxide agglomerated in curdy masses which settled very quickly. Sodium oleate tends to give emulsion of oil in water and it is not surprising therefore that emulsions of water in oil are rendered less stable. On the other hand, water could be very readily emulsified in the paints containing calcium oleate. In this case, both the paint and the calcium oleate tend to give emulsions of water in oil with the result that a stable emulsion is formed.



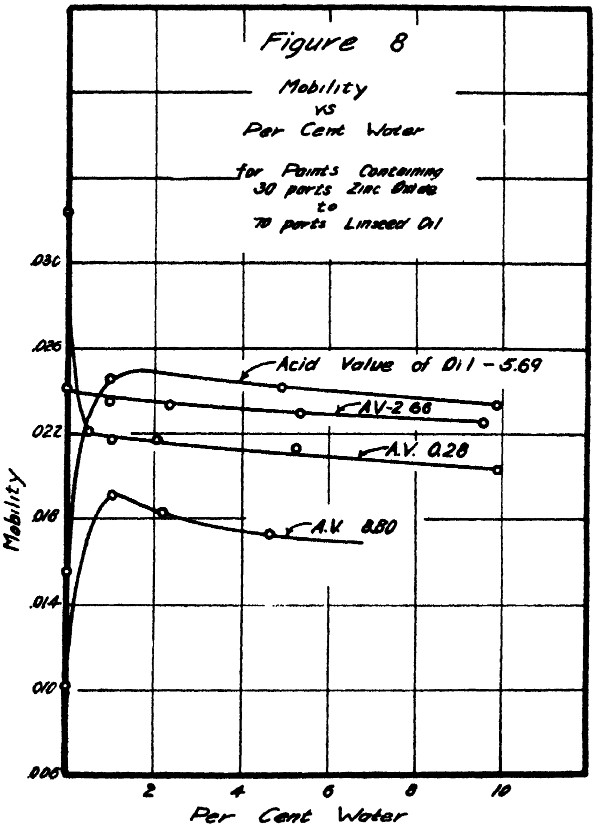
The water increases the yield value of these paints. The effect is qualitatively similar to that observed with paints which contained no soap. The first additions had a greater effect than later ones. For the same water content, the paints made with soap have a greater yield value than those without. That is, the effect due to the water and that due to soap are qualitatively additive. The mobilities of these paints are lowered by water, the effect being more pronounced with the first additions. The water does not have such a large effect as it does in those paints free of soap. The soaps counteract some of the drop in the mobility due to water, sodium oleate being more effective than the calcium oleate.

Joint Action of Water and Free Fatty Acids. Free fatty acids were prepared from linseed oil by saponifying the linseed oil by heating with alcoholic potash, distilling off the alcohol, liberating the free fatty acids by adding dilute sulphuric acid, and washing the separated acids thoroughly with water.



The acids thus obtained were but slightly darker than the original oil and had an acid value of 197.1. This free fatty acid was mixed with various portions of the linseed oil to give oils of the desired acid values. The pigment used for this work were: zinc oxide, white lead, and aluminum powder. The paints made with zinc oxide contained 30 parts of the pigment to 70 of the vehicle, those with white lead contained 60 parts of the pigment to 40 of the vehicle, while those made with aluminum powder contained 30 parts of the pigment to 70 of the oil.

The first method of incorporating the water was found satisfactory if the water was readily emulsified in the paint and was therefore adopted in the first part of the experimental work. It was found, however, that water could be emulsified somewhat more readily by shaking the mixture of paint and water than by merely grinding the two together. Accordingly, the following procedure for introducing water into these paints was adopted: About 30 to 40 cubic centimeters of the paint was placed in a 100 cc bottle, the desired amount of water was added, the mixture thoroughly shaken, and then allowed to stand for about one hour before being tested in the plastometer. The effect due to the air that may have been introduced into the paint during the shaking process was assumed to be negligible and paints prepared in this way were not evacuated a second time. The results are shown in Table IV and in Figs. 7 to 12.



The effect of water in these paints is more complex than in those paints made with the practically neutral linseed oil. Paints made with zinc oxide and low acid value oil showed an increase in the yield point and a decrease in mobility as the water content was increased. The effect of the free fatty acid alone in the linseed oil is to increase the yield value greatly. The presence of both water and free fatty acid results in changes in the plasticity depending on the conditions. If the acid value of the oil is 2.66, the effect of water is

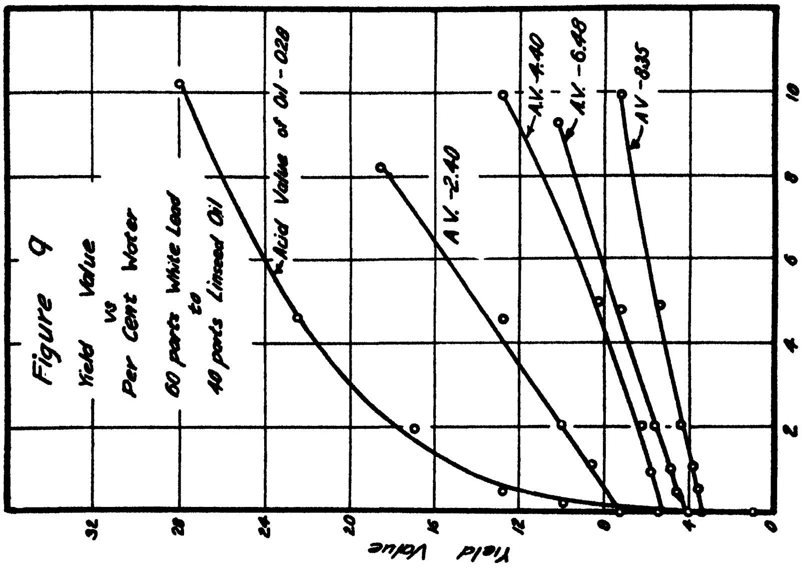


Figure 9
Yield Value
vs
Per Cent Water
60 parts White Lead
to
40 parts Linseed Oil
Acid Value of Oil -0.28
A.V. -2.40
A.V. -4.40
A.V. -6.48
A.V. -8.35
Yield Value
32
28
24
20
16
12
8
4
0
Per Cent Water
2
4
6
8
10

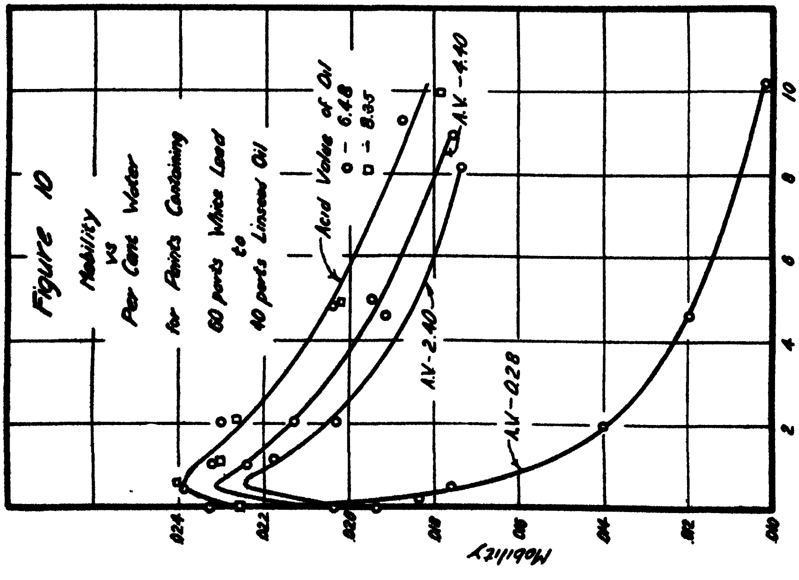


Figure 10
Mobility
vs
Per Cent Water
for Paints Containing
60 parts White Lead
to
40 parts Linseed Oil
Acid Value of Oil
○ - 6.48
□ - 8.35
A.V. -4.40
A.V.-2.40
A.V.-0.28
Mobility
.024
.022
.020
.018
.016
.014
.012
.010
Per Cent Water
2
4
6
8
10

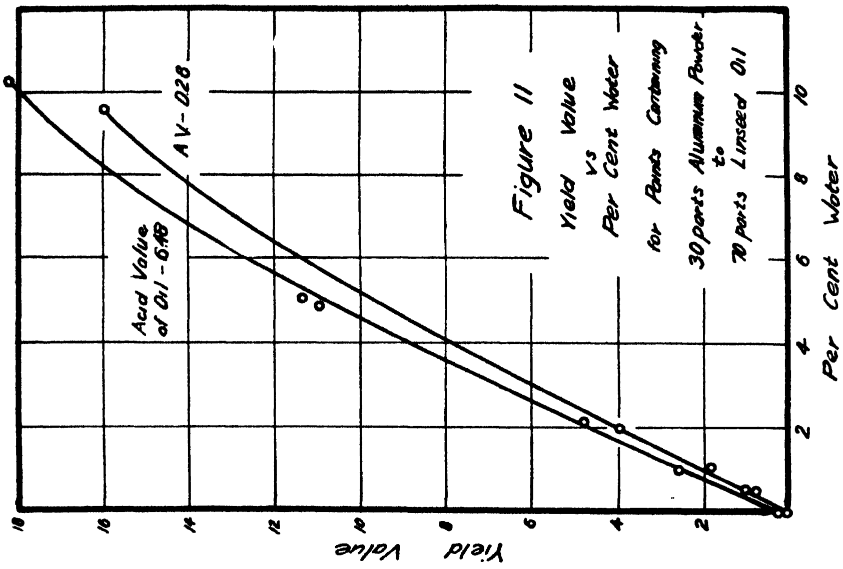


Figure 11
Yield Value
vs
Per Cent Water
for Paints Containing
30 parts Aluminum Powder
to
70 parts Linseed Oil

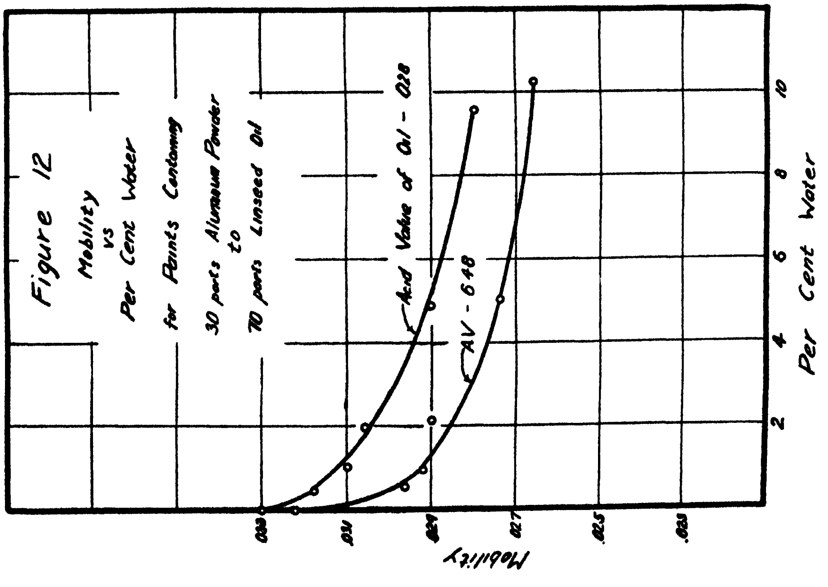


Figure 12
Mobility
vs
Per Cent Water
for Paints Containing
30 parts Aluminum Powder
to
70 parts Linseed Oil

TABLE IV

Effect of Water on Paints prepared from Linseed Oil of Varying Acid Value

Pigment	Acid Value of Oil	Per Cent of Water	Yield Value	Mobility
Zinc Oxide	0.28	0.00	4.8	0.0324
		0.51	12.4	0.0222
		1.03	15.0	0.0218
		2.00	15.8	0.0218
		5.27	17.2	0.0214
		9.89	19.6	0.0204
	2.66	0.00	10.9	0.0242
		1.00	11.3	0.0235
		2.23	11.6	0.0234
		4.32	12.5	0.0230
		9.57	13.2	0.0226
	5.69	0.00	25.0	0.0156
		0.99	11.5	0.0246
		4.91	13.2	0.0242
		9.90	13.4	0.0234
	8.80	0.00	28.0	0.0102
		1.06	12.0	0.0192
		2.24	14.0	0.0184
		4.65	15.5	0.0174
White Lead	0.28	0.00	1.0	0.0236
		0.22	10.0	0.0184
		0.49	12.8	0.0176
		2.00	17.0	0.0140
		4.62	22.5	0.0120
		10.22	28.0	0.0102
	2.40	0.00	7.2	0.0194
		1.14	8.5	0.0218
		2.06	10.0	0.0203
		4.59	12.7	0.0192
		8.21	18.5	0.0174
White Lead	4.40	0.00	5.4	0.0204
		1.01	5.8	0.0224
		2.06	6.2	0.0213
		5.00	8.3	0.0195
		9.95	12.8	0.0176

TABLE IV (Continued)

Effect of Water on Paints prepared from Linseed Oil of Varying Acid Value

Pigment	Acid Value of Oil	Per Cent of Water	Yield Value	Mobility
White Lead	6.48	0.00	4.0	0.0226
		0.49	4.5	0.0238
		1.03	4.8	0.0232
		2.02	5.6	0.0230
		4.81	7.2	0.0204
		9.28	10.2	0.0188
	8.35	0.00	3.4	0.0226
		0.58	3.6	0.0240
		1.08	4.0	0.0230
		2.10	4.4	0.0226
		4.92	5.4	0.0202
		9.94	7.2	0.0179
Aluminum Powder	0.28	0.00	0.0	0.0330
		0.51	0.8	0.0318
		1.04	1.8	0.0310
		2.00	4.0	0.0306
		4.90	11.0	0.0290
		9.60	16.0	0.0280
	6.48	0.00	0.2	0.0322
		0.57	1.0	0.0296
		0.98	2.6	0.0292
		2.16	4.8	0.0290
		5.09	11.4	0.0274
		10.25	18.2	0.0266

to increase but slightly the relatively high yield value due to the free fatty acids. However for paints made with linseed oil with an acid value of 5.69 and 8.80, the first addition of water has a very pronounced effect in lowering the yield value. A minimum value is obtained at about one per cent of water and further additions increase the yield value.

For paints made with zinc oxide and a practically neutral linseed oil, the effect of the water alone or of fatty acids alone is to increase the mobility. With an acid value of 2.66 for the oil, the mobilities are decreased but slightly on addition of water with the result that the mobilities are higher for these paints for the same water content than with those made with the low acid value oil. When the acid value of the oil is 5.69 the first additions of water tend to increase the mobility to a maximum value when about one per cent of water is present. Further additions lower the mobility again slightly. The paints made with this concentration of free fatty acid show the highest mobilities for any given content of water. When the acid value of the oil is 8.80, there is again a maximum in the mobility curve when about one per cent of water is present, but these paints all show a relatively low mobility.

With paints made with white lead, the effect of free fatty acids alone on the yield point is to increase it to a maximum at an acid value of 2.40 and then to decrease it continuously on addition of more free fatty acid. The lowest yield value is shown by the paint made with neutral oil and no water. For acid values of the oil of 2.40 and above, the effect of the water is to increase the yield value slightly, and for the same concentration of water, the yield value decreases as the acid value increases.

The effect of free fatty acids on the mobility of paints made with dry white lead is to decrease it to a minimum with an oil of acid value of 2.40 and then to increase it slightly with further additions of free fatty acid. For paints made with linseed oil of 2.40 and higher, the mobility increases to a maximum on addition of about one-half of one per cent of water and then decreases again. The mobilities are higher for the same water content in those paints made with oil of higher acid value.

The paints made with aluminum powder had practically the same yield value for the same amount of water when made with linseed oil of acid value of 0.28 or 6.48. Water increased the yield value in both cases. The mobilities of these paints decrease as more water is added, the values for the paints made with oil of acid value of 0.28 being slightly higher than those made with oil of acid value of 6.48.

Effect of Heating the Paint. The effect due to heating the paint was studied with mixtures made up with 30 per cent of zinc oxide and 70 of linseed oil (Lot 2). The paints were prepared as described and then heated for half an hour in an oil bath kept at a temperature of 150 to 160°C. To prevent any oxidation of the oil during the heating, a slow stream of nitrogen was passed through the flask. The following results were obtained.

TABLE V

Effect of Heating the Paint

Acid Value of Oil	Heat Treated	Yield Value	Mobility
0.28	No	4.8	0.0324
0.28	Yes	5.4	0.0332
8.35	No	31.0	0.0136
8.35	Yes	6.0	0.0274

With the paints prepared from the neutral linseed oil, the effect of heating the paint resulted in a slight increase in yield value and mobility. A very pronounced change occurs however with paint made with the oil of acid value of 8.35. The yield value is reduced almost to that for the paint made with the neutral oil while the mobility is increased to double its initial value.

That this effect is not due to any change in the linseed oil was shown by preparing paints from linseed oil that had been heated as described, cooled, and then used in preparing these paints. The plastic constants of these paints differed but little from those of paints prepared from untreated linseed oil of the same acid value.

As described in the first part of the experimental work, the effect of adding one per cent of water to a paint made with 30 parts of zinc oxide and 70 of linseed oil with acid value of 8.35 was to decrease the yield value and increase the mobility. This effect is very similar to that due to heat although not as marked. If the effect due to the water is the same as that due to heating the paint, the addition of water to a paint that has been heated should not result in lowering of the yield value and an increase in the mobility when approximately one per cent water is added. Water was added to a paint made with linseed oil of acid value of 8.35 and zinc oxide and heated as described above. The water had a similar effect in increasing the yield value and decreasing the mobility as in those paints made with the neutral oil.

Effect of Zinc Sulphate. The effect due to zinc sulphate in paints made with zinc oxide was studied with mixtures prepared with one part of anhydrous zinc sulfate, thirty of zinc oxide, and seventy of linseed oil of various acid values. The plastic constants for these paints were found to be practically independent of the zinc sulphate content for paints made with linseed oil of acid value as high as 8.35.

Effect of Free Fatty Acid and Soap. Paints were prepared with thirty parts of zinc oxide, seventy of oil, and two of calcium oleate as described previously. The results are shown in Table VI.

Table VI

Effect of Calcium Oleate on Paints prepared from Linseed Oil of Various Acid Values

Acid Value of Oil	Parts of Soap added	Yield Value	Mobility
0.28	0.0	4.8	0.0324
0.28	2.0	5.5	0 0300
2.40	0.0	10.4	0.0250
2.40	2.0	6.0	0.0308
8.35	0.0	31.0	0.0136
8.35	2.0	6.2	0.0288

The effect of the soap in the paint made with the oil of low acid value is to increase the yield value slightly and lower the mobility. However in the paint made with the oil of acid value of 2.40 the soap decreased the yield value and increased the mobility. The same thing was true in the case of the paints made with the oil of 8.35 although the effect was very much more marked. When this last paint is heated, the yield value is lowered still more and the mobility increased to practically the same value as those for the paints made with neutral oil and no water.

Discussion of Results

The results obtained with paints made with practically neutral linseed oil can be readily explained qualitatively. The effect of the water in always increasing the yield value and lowering the mobility is due to its tendency to emulsify in the paint and thus build up a structure in the paint. The amount of the increase in consistency depends on the type of pigment, the concentration of the pigment, and the concentration of water. The effect of sodium oleate and calcium oleate is to increase the yield value and decrease the mobility due to their gel structure in the paints. The sodium oleate has a more pronounced structure than the calcium oleate and so has a greater effect in increasing the consistency.

The presence of free fatty acids in the vehicle may affect the plasticity of the paints in various ways. With paints made with zinc oxide, the effect of the free fatty acids in the linseed oil is to increase the consistency of the paint very markedly. This is probably due to the interaction of the zinc oxide and the free fatty acids to give zinc soaps. The addition of anhydrous zinc sulphate to these paints has no appreciable effect; although as this is a soluble zinc salt, one would expect it to form soaps more readily than the zinc oxide and thus increase the consistency to a greater extent. Apparently the free fatty acids are able to react with the dry zinc oxide rather completely.

When the acid value of the oil is 8.35, there are several factors that can decrease the initial high consistency due to the free fatty acid. Water in small amounts tends to do this. Heating the paint for thirty minutes at a temperature of 150°C brought the plastic constants very close to that for the paints made with the neutral oil. The addition of two parts of calcium oleate was also found to have approximately the same effect as that due to heat. Another factor that tends to do the same thing is ageing which lowers the consistency.

With paints made with zinc oxide and linseed oil of high acid value, soaps are formed in relatively large amounts. The zinc soaps are insoluble in the linseed oil, but are probably dispersed to some extent by the free fatty acids present. That free fatty acids are adsorbed by the soap micelles has been shown by Arsen.[17] The high consistency of paints made with a high acid value oil is due to the soap micelles which are present as loose ramifying aggregates. Anything that will tend to precipitate out the soap and thus destroy the structure of the soap should result in a lowering of the viscosity of the paint.

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[17] Ind. Eng. Chem., **18**, 157 (1926).

With time more of the free fatty acids react with the zinc oxide to form soaps. The result is a gradual decrease in the concentration of the free fatty acids. The vehicle then loses its power to disperse the soaps which are precipitated out. The gel structure of the soap in the paint is thus broken down with a resulting decrease in the yield value and increase in the mobility. This is probably the change that occurs during the ageing of paints prepared with zinc oxide. Water is known to precipitate soaps from solution in organic liquids and its action in reducing the consistency of paints prepared from linseed oil of high acid value and zinc oxide can be explained on this basis. Thus calcium soaps are precipitated out as a flaky material from a clear benzene solution in the presence of a trace of moisture.[18] Also lead and zinc soaps in greases are unstable and will tend to precipitate out if water is present. The effect of heating the paint is due to the increase in the rate with which the free fatty acids react with the pigment to form soaps. The action is thus similar to that which occurs during ageing. The calcium oleate is effective in lowering the concentration of the free fatty acid due to its ability to adsorb these acids. The calcium soaps apparently have but little effect in changing the consistency even when dispersed in the vehicle.

This change in the structure of the soap micelles may also explain why turpentine is less effective in reducing the consistency of paints than some of the other thinners. It is known that zinc soaps are insoluble in neutral linseed oil and in naphtha and are soluble to some extent in free fatty acids and in turpentine.[15] The turpentine apparently has the power to disperse the zinc soaps into loose ramifying aggregates which tend to enmesh the vehicle and thus increase the consistency.

With paints prepared from white lead, the effect due to any free fatty acid is very much less marked than with paints made with zinc oxide. An increase in the acid value of the oil from 0.28 to 2.40 resulted in a slight increase in consistency probably due to the formation of a small amount of soap. Any further increase in the acid value of the oil resulted in a decrease in consistency due to the better wetting and dispersing power of the vehicle. Moreover the lead soaps differ from the zinc soaps in that they do not have the same tendency to coagulate or "lump".[15]

The result is that no very marked structure is built up in the paint with a resulting increase in consistency. Some soaps are however formed. With paints prepared with linseed oil of acid value of 2.40 or higher, the addition of one-half of one per cent of water results in an increase in mobility while further additions lowered the mobility. The ability of water to increase the mobility of these paints is substantiated by the fact that paints prepared from pulp-mixed white lead are said to have better working properties than those prepared from pan-dried white lead.

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[18] Wellman and Tartar: J. Phys. Chem., 34, 379 (1930).

Summary

1. Water added to a paint prepared from a practically neutral linseed oil increases the yield value and decreases the mobility; the amount of the effect depending on the type and concentration of pigment.

2. Sodium oleate and calcium oleate increase the yield value and decrease the mobility of a paint prepared from a neutral linseed oil, the effect being more pronounced for the sodium oleate.

3. Water added to a paint prepared from a practically neutral linseed oil and two parts of sodium oleate or calcium oleate increases the yield value and decreases the mobility.

4. With paints prepared from linseed oil and dry zinc oxide, the effect of free fatty acid is to very markedly increase the consistency. Small additions of water tend to offset part of this increase in consistency, the effect being most marked when one per cent of water is present and the acid value of the oil is relatively high.

5. With paints prepared from dry white lead and linseed oil, the effect of free fatty acids is relatively small. With paints prepared with oil of acid value of 2.40 or higher, the mobility has a maximum value when about one-half of one per cent of water is present; while the yield value increases slightly but continuously with water content.

6. The presence of anhydrous zinc sulfate has but little effect on the plastic constants of paints prepared from zinc oxide.

7. The increase in consistency in a paint prepared from zinc oxide due to the free fatty acids present in the vehicle can be practically completely offset by heating the paint for one-half hour at 150°C. The same result can also be obtained by the addition of two parts of calcium oleate in the paint.

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THE CATALYTIC OXIDATION OF CARBON MONOXIDE

BY J. C. W. FRAZER

Introduction

The catalytic oxidation of carbon monoxide is of interest largely because of the unusual and interesting properties of carbon monoxide. My interest in this subject began with the development some years ago of a catalyst which would bring about the complete oxidation of this gas at 0°C and below at an extremely rapid rate. The first catalyst which we developed consisted of manganese dioxide and silver oxide. Shortly after this we found it possible to prepare a catalyst equally good from manganese dioxide and copper oxide.[1] In both mixtures the manganese dioxide was readily recognized as the more active of the two constituents. Finally we found it possible to prepare an equally good catalyst from manganese dioxide alone[2] by using a method for its preparation which eliminated the possibility of contamination with adsorbed materials, particularly alkalies which manganese dioxide is so prone to adsorb from solution and from which it cannot be freed by ordinary methods of washing. Subsequently it was found possible to prepare finely divided cobaltic oxide[3] in a state of purity and of equal catalytic activity for the oxidation of carbon monoxide. Finally, Bennett[4] working in this laboratory, has succeeded in preparing so-called "nickelic oxide" finely divided and free from adsorbed materials and again the metallic oxide so purified has been found to be an extremely active catalyst for the reaction under consideration. In all three of these cases the essential characteristics of the catalyst are the existence of the metallic oxide in finely divided condition and free from adsorbed materials. In all three cases the use of other oxides and so-called "promoters," originally thought by many necessary to obtain catalysts of high catalytic activity, has lost its significance, freedom from "poisoning" impurities being much more important. Having carried the experimental work this far it became at once a matter of interest to see what degree of success would attend the preparation of catalysts from other metallic oxides in a pure and finely divided condition.

For this purpose a method was devised for electrolysing the impurities from the finely divided oxides suspended in water.[4] This was the only method which could be relied on to free many of these oxides from adsorbed materials. None of the seventeen oxides as prepared was found to be in the same class as catalysts for this reaction as the three already mentioned, although some of them as for example ferric oxide show some activity below 100°C.

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[1] Roger, Piggot, Bahlke, and Jennings: J. Am. Chem. Soc., 43, 1973 (1921).

[2] Whitesell and Frazer: J. Am. Chem. Soc., 45, 2841 (1923).

[3] Williams: Dissertation, Johns Hopkins University (1928).

[4] Dissertation, Johns Hopkins University (1930).

It appears on studying the properties of these highly active oxides that they are characterized by one common property which distinguishes them from the other oxides and to which we are inclined to ascribe their high catalytic activity. This property is their indefinite composition. They all behave as mixtures of more than one oxide which mutually dissolve to form solid solutions. This appears not to be true of the other oxides tested under the conditions of their use in these experiments. This property enables these oxides to function as catalysts over a wide range of oxygen pressure allowing them to give up or take on oxygen with great readiness, the oxygen as given up amounting essentially to nascent oxygen is activated and readily reacts with the carbon monoxide which is likewise probably activated by adsorption on the catalyst.

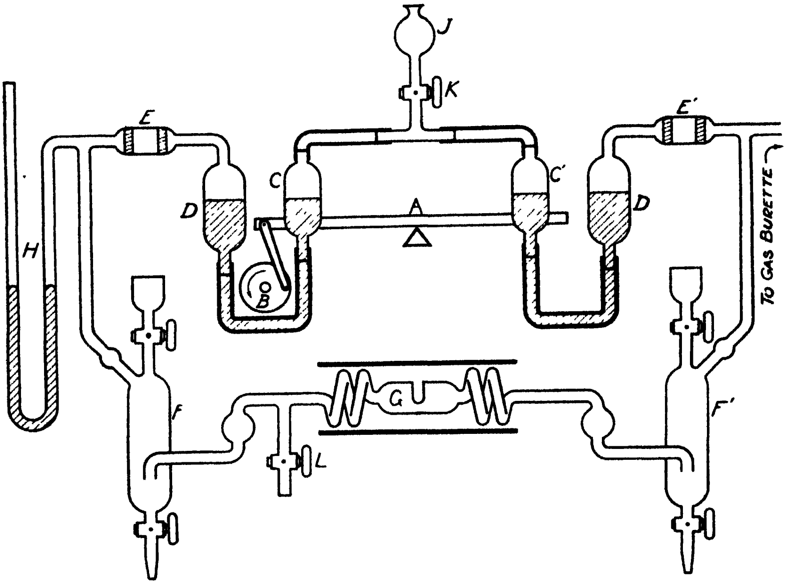

Fig. 1

This peculiar property was first studied in the case of finely divided manganese dioxide. English,[5] in an unpublished investigation, showed in this laboratory that finely divided manganese dioxide readily dissociated and the oxygen pressure in equilibrium with the oxide depended on the composition of the oxide.

English's apparatus shown in Fig. 1, consisted of a closed system. The part of this system containing the sample of oxide under investigation was kept in an electric furnace the temperature of which was regulated. At the beginning of the experiment the system was filled with pure nitrogen which was passed backward and forward at regular and frequent intervals over the oxide in the furnace. The mechanism by means of which this was accomplished is shown in the illustration referred to. Provision was made for keeping the temperature of the gas in contact with the oxide the same as that of the oxide and also for removing the water vapor given off from the oxide.

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[5] Dissertation, Johns Hopkins University (1922).

In order to follow the course of the reaction it is only necessary to know the capacity of the gas space, the original composition and weight of the oxide used. At intervals a sample of the gas was removed for analysis and the partial pressure of oxygen therein determined. After the oxygen determination the nitrogen was returned to the system or this could be done after restoring the amount of oxygen it contained when it was removed from the system. In this way the results given in the following series of curves, Fig. 2, were obtained. It will be seen that as oxygen is removed from the system and the oxygen content of the oxide diminished the dissociation pressure of the oxide diminishes. With each removal of oxygen the dissociation-pressure curve drops and finally approaches the lowest curve which is that of Askenasy[6] for the dissociation of pyrolusite after it has been strongly heated.

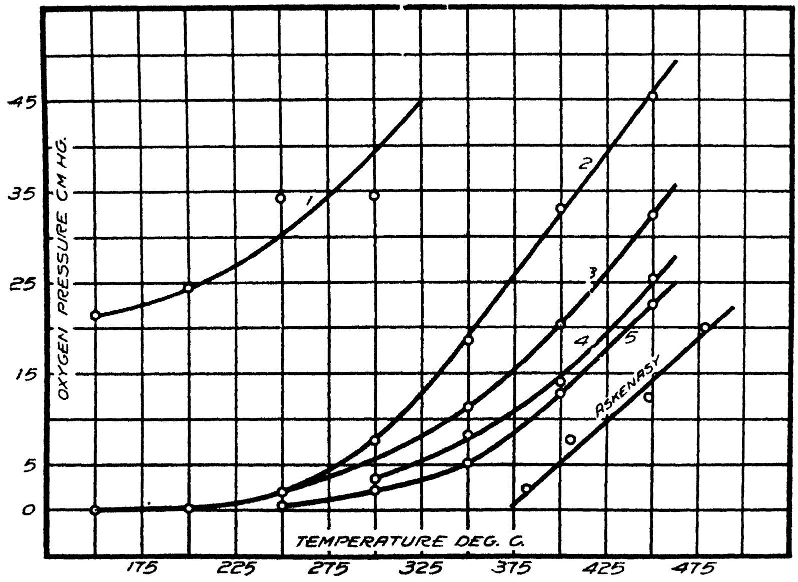

Fig. 2
Oxygen Pressure over 20 Gm. Fremy Oxide

In 1924, Weld[7] working in this laboratory made a much more careful study of the dissociation of manganese dioxide using a static method. The apparatus used is shown in Fig. 3. The oxide was kept for long periods of time at constant temperature, especially at the low temperatures. This was accomplished simply by using various pure liquids with appropriate boiling points to fix and maintain the desired temperatures. The results obtained are shown for manganese dioxide of a certain known composition in the following series of curve, Figs. 4 and 5.

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[6] Askenasy and Klonowski: Z. Elektrochemie, **16**, 107 (1910).

[7] Dissertation, Johns Hopkins University (1924).

The two remaining oxides, "nickelic" oxide and cobaltic oxide have been more recently studied by Le Blanc and Sachse.[8] In both cases there is ample evidence that both of these oxides show a similar variable oxygen content and give up or take up oxygen continuously according to conditions.

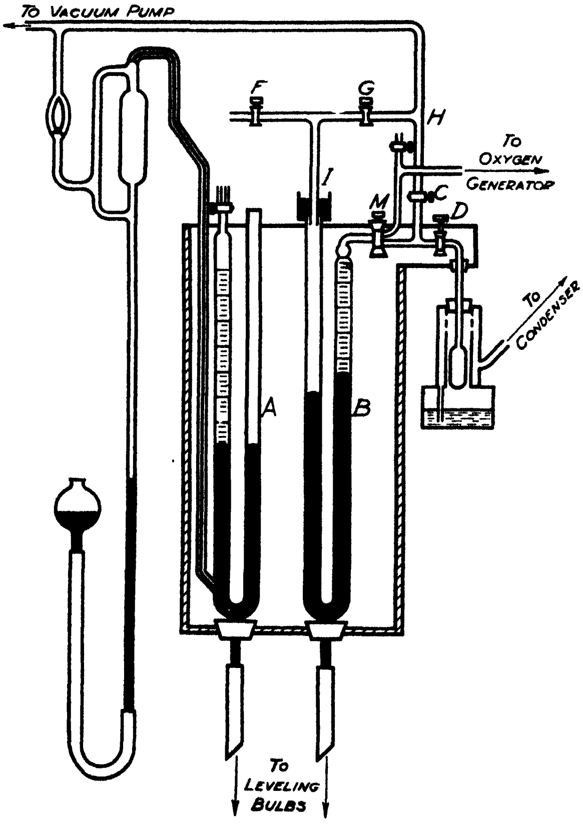

Fig. 3

It is assumed that this property is responsible for the very great catalytic activity of these oxides and distinguishes them in their catalytic behavior from other metallic oxides investigated and gives a mechanism by means of which oxygen is activated at such a surface.

Owing to the fine porosity of these oxide catalysts they are also characterized by their ability to condense vapors within their pores. For example, unless water vapor is removed from the gases in contact with them these catalysts lose their catalytic properties through capillary condensation of water within the porous oxide. In testing the catalytic properties of these oxides they and the gases passing over them are carefully dried.

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[8] Z. Elektrochemie, 32, 58, 204 (1926); Z. physik. Chem., 142, 151 (1929).

The effect of traces of water vapor on many reactions is well known. This effect on the oxidation of carbon monoxide has been noted and carefully studied by Dixon and others.[9]

The investigations of greatest interest to us here are those which show the effect of small traces of water vapor on the explosibility of a mixture of carbon monoxide and oxygen and also on the rate of flame propagation in such an explosive mixture.

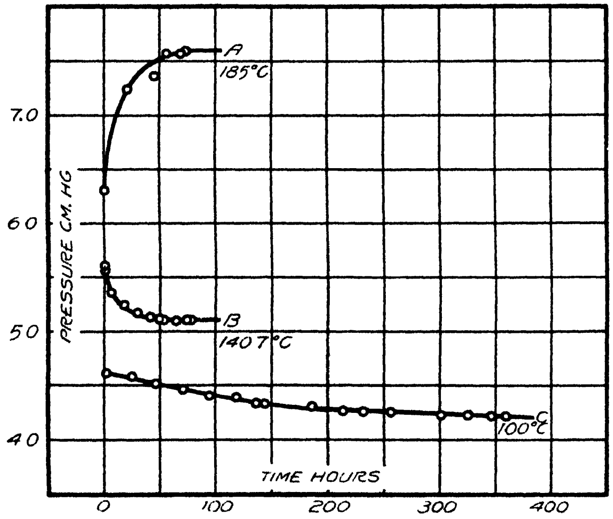

FIG. 4

It was thought that a trace of water on these catalysts might exert a similar effect on their activity. In 1925 Blitch[10] in this laboratory undertook to investigate this point. A sample of active manganese dioxide was heated for one week in an all glass apparatus in a current of oxygen dried over phosphorus pentoxide. At the end of this time the sample showed its former activity. It was then dried similarly for another week at 240°. At the end of this time it still retained its activity. It was then dried continuously for another week at 300° and at the same time the apparatus frequently evacuated. At the end of the experiment it had apparently lost none of its original activity.

More recently Bone[11] has investigated the effect of extreme drying on the catalytic oxidation of carbon monoxide using such substances as copper and nickel oxides and metallic gold and silver. In all the cases the first effect of drying was an increase of catalytic activity due to the removal of the water condensed by capillarity as discussed above. In the experiments with gold (at 250°) and silver (at 365°) the drying was carried to great extremes and the remarkable fact was observed that the catalytic action practically ceased. The introduction of small amounts of water was sufficient to restore the high catalytic activity. The velocity constant in the case of gold was 0.0155 (moist) and 0.00045 (dry). In the case of the experiment with silver the constant varied from 0.1208 to 0.0039. This apparent discrepancy in the effects of extreme drying on the catalytic activity of extremely active catalysts such as manganese dioxide on the one hand and poor catalysts such as metallic silver and gold on the other may be reconciled if we assume that in the one case oxygen is activated and the reaction catalysed is $2CO + O_2 \rightleftarrows CO_2$ and where the effects of extreme drying are negligible while in the other case which is almost completely inhibited by extreme drying the reaction catalysed is the water-gas reaction

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[9] Dixon: Brit. Assocn. Adv. Sci. Repts., 503 (1880); Phil. Trans., **175**, 617 (1884); Baker: J. Chem. Soc., **47**, 349 (1885); Phil. Trans., **179**, A 571 (1888); Bone and Weston: Proc. Roy. Soc., **110A**, 615; Bone, Frazer, and Newitt: 634 (1926); Fenning: Phil. Trans., **225A**, 31 (1926).

[10] Dissertation, Johns Hopkins University (1925).

[11] Proc. Roy. Soc., **112A**, 474 (1926).

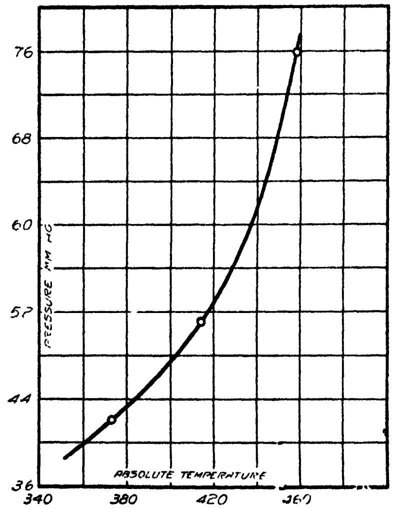

FIG. 5

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

$$H_2 + O_2 \rightleftarrows H_2O$$

The catalytic oxidation of carbon monoxide is of technical interest in connection with the risks which industrial workers in several fields run from exposure to dangerous concentrations of this gas. A great step forward in this direction was taken during the war by the production of catalysts of the Hopcalite type for use in gas masks. When properly used these masks give complete protection against carbon monoxide. Many suggestions have been made to eliminate carbon monoxide from the exhaust gases of internal combustion engines. At the present time, however, there is no device of this kind available, but we have demonstrated that it is possible to produce a catalyst which will completely remove carbon monoxide from the exhaust gases of automobiles and some of these catalysts have been tested in a temporary device through which all of the exhaust gases were passed. The longest of these was a regular road test covering a distance of 1500 miles. Whether the possibilities of such catalysts can be fully utilized and applied in a commercial way remains shortly to be seen as work on the mechanical applications are now well under way.

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A STUDY OF THE INFLUENCE OF HYDROLYSIS TEMPERATURE ON SOME PROPERTIES OF COLLOIDAL FERRIC OXIDE

IV. Variation of Density and Relative Viscosity with Sol Concentration

BY GILBERT H. AYRES AND C. HARVEY SORUM*

Introduction

References in the literature to the relation between density and concentration in colloidal systems are not numerous. Linder and Picton[1] studied some of the physical properties of As_2S_3 sols and found that the relation between specific gravity and dilution was linear, which is not the case with solutions of metallic salts. Dumanskii[2] prepared ferric hydroxide sols by the dialysis of ferric chloride solution saturated with ammonium carbonate. After standing for one year and then filtering through collodion, the density of the dispersed phase was determined by the use of the formula:

$$A = B + C - C/xd$$

where the symbols have the following significance:

A = weight of solution
B = weight of solvent
C = weight of colloid
x = density of colloid
d = density of filtrate

Dumanskii found that at 0°, x = 4.704, and since this was not the same as the value for the density of precipitated iron oxide, he concluded that the colloid was a mixture of oxide and chloride. He apparently took no consideration of the possibility of hydration of the disperse phase.

Wintgen[3] studied the density and refraction of colloids; he found the density (or its reciprocal, the specific volume) to be a linear function of the concentration. For colloidal iron hydroxide he gives the equation:

$$v = 1.00296 - (0.0065071\ C)$$

where v is the specific volume and C is the weight percent of dispersed phase. When $C = 100\%$, $v = 1.00296 - 0.65071 = 0.35225$, and d (the density) = $1/v = 1/0.35225 = 2.84$ for the disperse phase. This value is smaller than the density of the precipitated material, the difference being ascribed to the hydration of the dispersed particles.

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* The authors wish to express their thanks to Dr. J. H. Walton for many valuable suggestions during the course of this investigation.

[1] Linder and Picton: J. Chem. Soc., 67, 71 (1895).

[2] Dumanskii: Kolloid-Z., 8, 232 (1910).

[3] Wintgen: Kolloidchem. Beihefte, 7, 251 (1915).

Since the sols with which this study is concerned had given pronounced evidence of hydration[4], it was deemed advisable to study the density of the sols prepared at different temperatures, as well as the variation of density and relative viscosity with concentration.

Experimental Methods

For this study samples of the original stock solutions were diluted with distilled water to make series of varying iron oxide content (concentration expressed in grams of iron oxide per liter).

The relative viscosity of these diluted sols was determined following the same technique as previously described.[4]

Density determinations were made by means of a 10 cc. pyknometer; the pyknometer was filled with the sol which had been brought previously to the temperature of the thermostat, and the filled pyknometer allowed to stand in the thermostat for ten minutes; it was then removed, dried with a clean towel, and allowed to stand in the balance case for ten minutes, at which time the weighing was made. The pyknometer was calibrated with distilled water following the same procedure. The method just described was used in making all of the density determinations which were required in calculating the relative viscosity.

Results

Tables I to VI show the results of some typical determinations.

TABLE I

Variation of Density and Relative Viscosity with Concentration

Sol No. 42

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
0.5	0.9975	1.003	2.0	.9984	1.019
1.0	.9979	1 009	2 5	.9992	1.025
1.5	.9983	1.012	3.0	.9998	1.030

TABLE II

Variation of Density and Relative Viscosity with Concentration

Sol No. 45

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
1.0	0.9975	1.002	3.5	1.0002	1.009
1.5	.9983	1.004	4.0	1.0005	1.012
2.0	.9990	1.006	4.5	1.0009	1.013
2.5	.9993	1.006	5.0	1.0014	1.015
3.0	.9998	1.007			

[4] Ayres and Sorum: J. Phys. Chem., 34, 2826 (1930).

TABLE III

Variation of Density and Relative Viscosity with Concentration

Sol No. 58

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
0.5	0.9974	1.004	2.5	.9993	1.018
1.0	.9980	1.007	3.0	.9998	1.021
1.5	.9984	1.011	3.5	1.0001	1.025
2.0	.9988	1.014			

TABLE IV

Variation of Density and Relative Viscosity with Concentration

Sol No. II

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
1.0	0.9979	1.003	3.5	.9999	1.019
1.5	.9983	1.007	4.0	1.0003	1.023
2.0	.9987	1.012	4.5	1.0007	1.026
2.4	.9990	1.013	5.0	1.0011	1.030
2.8	.9993	1.015	5.84	1.0018	1.038
3.0	.9994	1.017			

TABLE V

Variation of Density and Relative Viscosity with Concentration

Sol No. III-C

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
1.0	0.9978	1.003	4.0	1.0005	1.013
2.0	.9988	1.007	5.0	1.0014	1.016
3.0	.9998	1.010			

TABLE VI

Variation of Density and Relative Viscosity with Concentration

Sol No. IV

Conc. g./l.	Density	Rel. Viscosity	Conc. g./l.	Density	Rel. Viscosity
1.0	0.9976	1.003	6.0	1.0026	1.050
2.0	.9987	1.005	8.4	1.0049	1.099
4.0	1.0010	1.019			

Fig. 1 shows the plot of density against sol concentration for two sols which represent the maximum variation observed; these two sols were prepared at the same temperature, namely, 100°. All of the sols studied showed a linear relation between density and concentration. The temperature of preparation of the sol had no detectable influence on the density of the system. The densities of 17 different sols, prepared at temperatures ranging from 100° to 140° and containing 2.0 g. of ferric oxide per liter, were determined; the mean density (25°) was 0.9988, the maximum deviation from the mean being ± 0.0002.

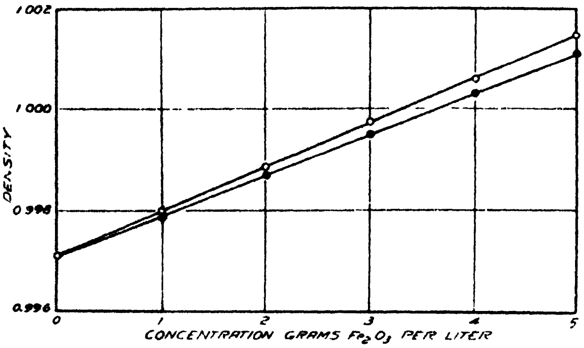

Fig. 1

○ Sol No. III-C
● Sol No. II.

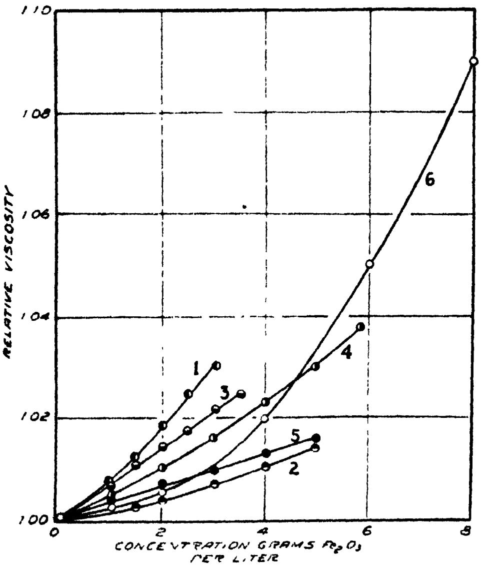

Fig. 2

The curves in Fig. 2 are plotted from the data of Tables I to VI.

Discussion

In speaking of sols such as those of Fe_2O_3 and Al_2O_3 Freundlich[5] says: "In all cases the viscosity increases in the region of small concentration *linearly with the content of the disperse phase.* The linear rise is confined to small concentration. For higher ones the viscosity-concentration curve is decidedly convex towards the axis of concentration."

Inspection of the curves in Fig. 2 shows that a linear relation is not observed in all cases. Of the six curves shown, only two exhibit the linear relation; in three other cases the viscosity-concentration curves are slightly convex towards the concentration axis, while in the other case the convexity towards the concentration axis is very pronounced.

It is of interest to note that the sols indicated as Nos. II, III–C and IV were prepared and dialyzed under conditions as nearly identical as possible; yet the curves are quite different in form: Sol No. II gives a curve which is slightly convex; Sol No. IV gives a curve which is decidedly convex; while the curve for Sol No. III–C shows a linear relation. It would seem, therefore, that a generalization as to the form of the viscosity-concentration curve in the case of colloidal ferric oxide is impossible.

It is somewhat difficult to interpret what Freundlich means by the "region of small concentration." The most concentrated sol used in these concentration studies contained 8.4 grams of iron oxide per liter, which is only 0.84% of disperse phase. In the case of Sol No. IV the curve shows a decided convexity even between the concentration of 2.0 and 4.0 grams per liter, corresponding to 0.2% and 0.4% of disperse phase.

Summary

1. The density of ferric oxide sols varies linearly with the concentration of the dispersed phase.

2. The density is not influenced by the temperature of preparation of the sol.

3. No generalization can be drawn regarding the shape of the viscosity-concentration curve, even at low concentrations of dispersed phase, say up to 0.5%. In some cases the relation is linear, while in others the curve is slightly or markedly convex towards the axis of concentration.

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[5] Freundlich: "Colloid and Capillary Chemistry," 367 (1926).

SOLUBILITIES IN THE SYSTEM WATER-IODINE TO 200°

BY F. C. KRACEK

1. Iodine dissolves in water to a limited extent only, but in aqueous solutions of iodides, particularly in KI, and RbI, its solubility is unusually high. This apparently abnormal solubility, taken together with other criteria, has led to a wide acceptance of the view that iodine combines with these salts in solution to form polyiodides. Such compounds, when they exist, should be capable of crystallizing from their solutions under the proper conditions, and hence, a phase rule study is obviously the most direct way of attacking the problem. The system water-iodine-potassium iodide was selected, principally because potassium "polyiodides" have figured extensively in the literature,[1] and secondly, because potassium iodide can be obtained in abundance, and in a state of high purity. The first measurements made have dealt with the three binary systems water-iodine, water-potassium iodide and iodine-potassium iodide, which form the boundaries of the ternary system. The results for the binary system water-iodine are communicated in this article.

2. Previous measurements of the solubility of iodine in water, summarized in Table I, end at 60°. The solubility is small, and increases moderately

TABLE I

Previous Reliable Values for the Solubility of Iodine in Water

t°C	Per cent Iodine		Reference
	weight	mol	
0.0	0.0162	0.00115	Jones and Hartmann: J. Am. Chem. Soc., **37**, 241 (1915).
18.0	.02764	.001962	Hartley and Campbell: J. Chem. Soc., **93**, 741 (1908).
25.0	.03394	002409	Hartley and Campbell: op. cit.
25.0	.03403	.002416	Sammet: Z. physik. Chem., **53**, 641 (1905).
25.0	.03386	.002404	Jakovkin: Z. physik. Chem., **18**, 585 (1895).
25.0	.03403	.002416	Noyes and Seidensticker: Z. physik. Chem., **27**, 357 (1898).
35.0	.04660	.003309	Hartley and Campbell: op. cit.
45.0	.06472	.004596	Hartley and Campbell: op. cit.
55.0	.09220	.006549	Hartley and Campbell: op. cit.
60.0	.10560	.007503	Sammet: op. cit.

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[1] See article by Grinnell Jones in J. Phys. Chem., **34**, 673 (1930) for a summary of published work on this question; see also Briggs, Greenawald and Leonard: J. Phys. Chem., **34**, 1951 (1930), which was published while this paper was in proof.

rapidly with temperature, but it is evident that the solubility curve must be of a special type in order to reach 100 per cent at 113.7°, the melting point of iodine. A preliminary experiment confirmed the supposition that two liquid layers are formed at higher temperatures, and subsequent measurements have established the course of the solubility curve for solid iodine to 112.3°, the quadruple S-L_I-L_{II}-V invariant points, and the curves for the mutual miscibility of the liquid layers from 112.3° to beyond 200°. The critical solution temperature, estimated to be about 300°, could not be reached because of the extremely high vapor pressure developed by the system.

Experimental

3. *Method of Solubility Determination.* Because of the volatility of both water and iodine, the usual methods of measuring solubility can not be applied to this system at the higher temperatures. The method adopted for this work was that of rotating, in a regulated air bath, tubes in which known amounts of the constituents were sealed up, and noting the temperature at which the last trace of the dissolving phase disappears. The temperatures were kept constant at each stopping point long enough to assure equilibrium being attained, particularly in the neighborhood of the point of disappearance of the phase which is dissolving in the solution. This equilibrium method of solubility determination is analogous with the quenching method used so extensively in this Laboratory in silicate work, and can be recommended as an excellent method for all cases in which the solubility exceeds a certain arbitrary minimum value, since the method depends upon visual detection of the last traces of the dissolving phase; in the case of crystals, the uncertainty is of the order of less than 0.1 mg of material. The refinement of the method depends upon accurate knowledge of the weights of substances sealed in the tube, and on sufficiently sensitive temperature control. With modern facilities, neither of these requirements offers any difficulties.

4. The tubes employed were made from Pyrex tubing 11 mm outside diameter, 1.2 mm wall thickness. No attack on the glass was noticeable, and the mechanical strength of such tubes appears to be sufficient to withstand in excess of 40 atm internal pressure. A constriction was blown in the tubes to facilitate sealing when filled, the open end serving as a funnel for the introduction of the materials.

Iodine was weighed into a tared tube in the desired amount, water was then added and the tube sealed. The drawn-off portion was then weighed together with the sealed tube, to obtain the weight of water. All weighings were made to 0.1 mg purely as a matter of routine.

The electrically-heated air bath was regulated by a special potentiometer controller of a standard commercial type, using a five-junction copper-constantan thermocouple. The sealed tube was attached by clips to a fan, rotated at about 40 r.p.m., which kept the air in the bath in motion. Double-walled glass windows provided a means of observing the tube during the course of an experiment. The temperature inside the air bath was read on a separate potentiometer, with a calibrated copper-constantan single junction thermocouple. The temperature control was sensitive to ±0.1° at all temperatures employed; small erratic fluctuations of temperature, due to eddies in the current of air in motion past the bare thermocouples, were of relatively small consequence in view of the great differences in heat capacity between the solubility tubes with their contents, and the air.

5. *The Method of Determination of the Fixed Points*, namely, the melting point of iodine, and the temperature at which solid iodine is in co-existence with the two liquid phases and vapor, differed from that just described. These two temperatures are only a little over 1° apart, and since liquid iodine is a very dark, relatively viscous liquid, totally non-transparent, the rotating tube method can not give correct results.

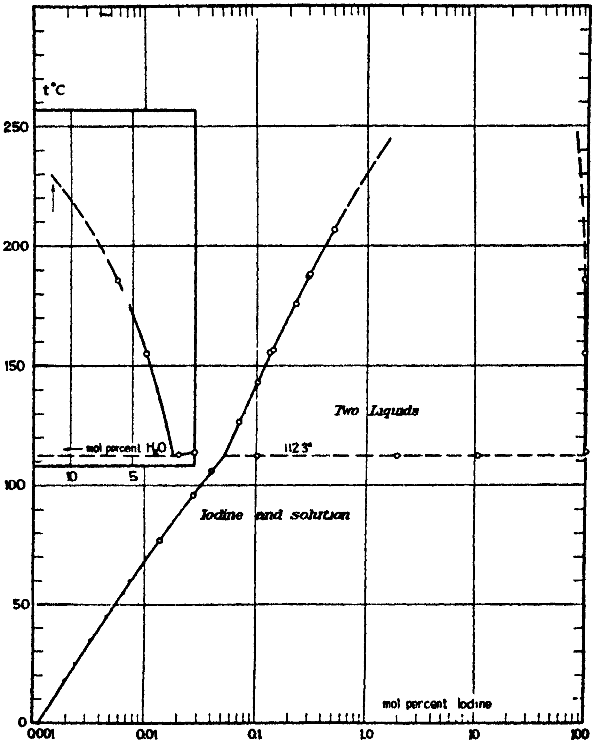

FIG. 1
Logarithmic graph of the solubility relations in the system water-iodine.
Inset figure: Solubility relations in the iodine end of the system.

It was advantageous to determine these points by thermal analysis in sealed tubes, since iodine is appreciably volatile at its melting point, and the S-L_I-L_{II}-V temperature is above the normal boiling point of saturated iodine solutions. The tubes selected for this purpose were of the type previously employed in the study of the polymorphism of potassium nitrate,[1] being provided with a re-entrant well for the insertion of the thermocouple. To obtain good temperature distribution the tubes were supported within a heavy copper block placed in the furnace, with a uniform air space between the copper block and the tube, the heat being carried to the tube only by radiation and air convection. A reference couple was placed in a well in the copper block, and differential heating curves at a controlled rate of *ca* 0.5° per minute were taken, alternately reading the temperature of the charge in the tube, and the differential temperature of the charge with reference to the block. The thermocouples used were of copper-constantan, calibrated with accepted standards.

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[1] F. C. Kracek: J. Phys. Chem., 34, 225 (1930).

6. *The Experimental Results.* The results obtained with solutions are collected in Table II.

TABLE II

Determined Values of Solubilities in the System Water-Iodine

Expt. No.	Iodine g	H_2O g	rw[1]	rm[1]	Per cent Iodine wt	Per cent Iodine mol	t°C
			A. Solid Phase: Iodine				
7	0.0091	4.6561	0.00195	0.000139	0.195	0.0139	77.1
6	.0136	3.5071	.00388	.000275	.386	.0275	96.0
5	.0258	4.5805	.00563	.000400	.560	.0400	106.1
11	17.2313	0.0161			.093*	1.30*	113.
			B. Two Liquids; Aqueous Layer				
4	0.0423	4.2915	0.00986	0.000700	0.976	0.0699	126.5
3	.0530	3.6732	.01443	.001024	1.422	.1023	143.2
1	.0757	4.0712	.01859	.001319	1.825	.1317	155.4
8	.0733	3.6907	.01986	.001409	1.947	.1407	156.4
2	.0973	3.0594	.03180	.002257	3.082	.2252	175.9
10	.1630	3.9170	.04161	.002953	3.995	.2944	187.4
9	.1731	4.0224	.04303	.003054	4.125	.3045	188.4
15	.2764	3.9182	.07054	.005006	6.589	.4981	206.7
			C. Two Liquids; Iodine Layer				
14	16.3529	0.0472			0.288*	3.91*	155.
13	21.1455	.0998			.470*	6.24*	186.
12	15.1964	.1407			.917*	11.54*	>225.

[1] rw = grams of iodine per gram of water.
rm = mols of I_2 per mol of water; H_2O = 18.0154, I_2 = 253.86.

* weight and mol per cent of water.

7. The melting point of iodine was determined to be 113.7°, and the invariant $S\text{-}L_{I}\text{-}L_{II}\text{-}V$ temperature 112.3°. The composition of the aqueous layer at this temperature, 0.0517 mol per cent iodine, equivalent to 7.29 g iodine per 1000 g water, was determined with sufficient precision by noting the point at which the solubility curve for solid iodine intersects the immiscibility curve, in a large scale logarithmic plot, shown in Fig. 1. The logarithmic plot is to be preferred in this case, since it separates the points on the aqueous solubility curves, and since it serves as a check on the relative

accuracy of determination of the data in this region. Moreover, the slope of the solubility curves above and below the S-L_I-L_{II}-V point in the logarithmic plot is such that the point of intersection is more definite than in the usual percentage graph. It will be seen that the data obtained in this investigation form a smooth continuation of the previously known curve.

8. The composition of the iodine-rich layer at the invariant S-L_I-L_{II}-V temperature was deduced graphically, as shown in the inset diagram in Fig. 1. The immiscibility curve meets the liquidus curve of iodine at 1.7 mol per cent H_2O (corresponding to 0.12 weight per cent H_2O), at a sharp angle. The liquidus curve of iodine then rises from this point to 113.7° at 100 per cent iodine.

9. The location of the water-iodine eutectic can be estimated from the known value of the solubility at 0°. If we take Jones and Hartmann's (op. cit.) value of 0.000638 mols I_2 per liter, and 1.86° for the molar freezing point depression, we obtain the temperature of the eutectic as −0.00119°. This is so near the melting point of ice that no experimental determination of the point can be realized, principally because iodine dissolves very slowly at 0°.

Table III contains a summary of the invariant points in the system.

TABLE III

Invariant Points in System Water-Iodine

Type	Solution, mol per cent Iodine	t°C
Ice → water, melting	0.0	0.0
Ice + solid iodine eutectic	0.00115	−0.0012
S-L_I-L_{II}-V,		
aqueous layer	0.0517	112.3
iodine layer	98.3	112.3
Critical solution point	——	*ca.* 300.
Iodine, melting	100.0	113.7

Discussion

10. These results are of interest from more than one viewpoint. First, and perhaps the more fundamental point of interest is, that aside from the intrinsic value of these data in establishing the previously uninvestigated formation of liquid layers in the system, we have here a plausible explanation for the anomalous behavior of polycomponent aqueous systems containing salts and iodine. It is a necessary consequence of the phase relations that the region of immiscibility must extend into the polycomponent systems, and since the immiscibility extends practically across the whole binary system, the effect in any polycomponent system will be large. Such solutions deviate so largely from ideal behavior that the ordinary laws of solutions lose much of their significance, and many deductions hitherto made from them for such systems must fail completely. In a ternary system, the S-L_I-L_{II}-V surface slopes down from the horizontal line at 112.3° in the binary system, and meets the liquidus curve of iodine at concentrations dependent upon the third component present. Thus, it is not surprising to find that at 25°, according

to Parsons and Whittemore,[1] the aqueous solution saturated with iodine and KI contains only *ca.* 6 wt per cent water.

11. A somewhat minor interest attaches to the extension of solubility studies into regions above atmospheric pressure, by the use of the sealed tube method. The method is old,[2] but very little use has been made of it in the past for exact work, principally for lack of facilities in maintaining constant temperatures in the neighborhood of any given point within the region studied. Granted that this requirement is satisfied, the method is convenient, moderately rapid, and more accurate than any other widely applicable method suitable for investigations at temperatures above the normal boiling point in the system studied.

12. Another point of interest lies in the relation of this system to the systems water-chlorine and water-bromine, studied by Bakhuis Roozeboom,[3] who showed that in both systems there are formed immiscible liquid layers, but that the solid phase in contact with the immiscibility region in each case is a hydrate instead of crystals of the element. The quadruple S-L_I-L_{II}-V point in the chlorine system is at 28.7° (m. p. of chlorine −103°), in the bromine system it is at 6.2° (m. p. of bromine −7.3°); in the iodine system the solid phase is pure iodine, and the temperature is 112.3°, just below the m.p. of iodine. The aqueous layer at the invariant point contains 0.915, 0.407 and 0.0517 mol per cent Cl_2, Br_2 and I_2 respectively, whereas the halogen-rich layers contain 99.5 mol per cent Br_2 and 98.3 mol per cent I_2 respectively (the composition is unknown for the chlorine system). The immiscibility region extends almost entirely across each of these systems. Of particular importance is the magnitude of the vapor pressures in these systems. In the chlorine system the vapor pressure of the saturated solutions is much less than the vapor pressure of chlorine; in the bromine system it exceeds the sum of the vapor pressures of bromine and water; so we may predict that in the water-iodine system the vapor pressure also exceeds the sum of the vapor pressures of the components.

Summary

Water-iodine solutions above 112.3° form two liquid layers, the mutual solubility increasing with temperature. The solubility curves were determined to temperatures above 200°. Below 112.3° the solutions are saturated with solid iodine. The composition of the liquid layers at the invariant temperature is 0.0517 and 98.3 mol per cent I_2 respectively.

Geophysical Laboratory,
Carnegie Institution of Washington,
July, 1930.

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[1] Parsons and Whittemore: J. Am. Chem. Soc., **33**, 1933 (1911).

[2] F. Guthrie: Phil. Mag., **18**, 105 (1884); W. Alexejeff: Ann. Physik, **28**, 305 (1886); more recently used extensively by N. V. Sidgwick and co-workers, see J. Chem. Soc. from 1911 on.

[3] Bakhuis Roozeboom: Rec. Trav. chim., **3**, 59, 73 (1884); **4**, 69, 71 (1885); Z. physik. Chem., **2**, 449 (1888).

NOTE ON A SIMPLE ONE-PIECE ELECTRODIALYSIS APPARATUS

BY L. REINER

Since electrodialysis has developed into a widely used laboratory method, a simple apparatus may have general interest. The apparatus previously used generally has been put together from three pieces corresponding to the three chambers of the common type of electrodialysis apparatus. This procedure is time consuming and also has the disadvantage that one must depend on rubber washers, and use some kind of clamp or device to keep the parts together. A simple apparatus has been described[1] which avoids these inconveniences. Practice with this apparatus, however, suggested the need of a membrane support. Dr. Prausnitz (Jena) suggested the use of Jena-glass filter plates as a support for collodion membranes. I then designed the apparatus described below. It was prepared in different sizes by the Schott works in Jena.

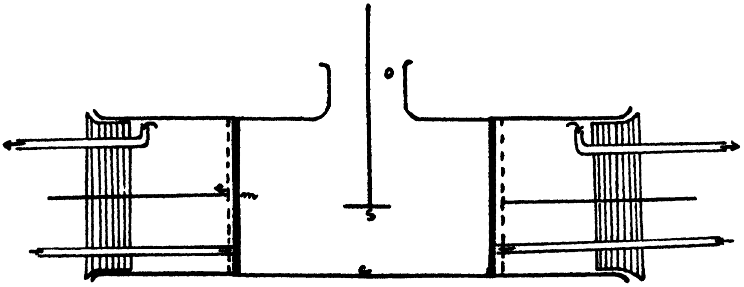

FIG. 1

A glass cylinder (c) has two filter plates (m) (medium porosity) sealed in at a distance of 8-10 cm. from each other, thus forming a cell, which is the middle cell of the electrodialysis apparatus. This middle cell has an opening (neck) at O to receive the stirrer (s). The two ends of the cylinder are closed with rubber stoppers containing the electrodes (e) and inlet and outlet for circulating water. Platinum gauze or platinized glass can be used as anode, and copper or nickel gauze as cathode. Stirring in the electrode chambers does not seem to be necessary, because the circulation of water can be made fast enough to provide the necessary mixing and quick diluting of the alkali and acid produced. If metal gauze is used the mesh should be wide enough not to prevent mixing. In the case of platinized glass electrodes, a daisy shape, i.e., a petal-like aster of blades, was used for the same purpose.

As membrane, ether-alcohol collodion or acetic acid collodion was used. Coating is made in the usual manner as for the preparation of ultra-filters.

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[1] Reiner: Kolloid-Z., 40, 123 (1926).

It is advisable to coat both membranes at the same time, filling the whole apparatus with the collodion solution and pouring it off only when the first drops of the solute appear on the back sides of filter plates. After sufficient drainage the whole apparatus is put in water for about 5 minutes, then the collodion is scraped off from the glass wall. This is necessary because the shrinking of the collodion connecting the two membranes may tear it off the filter plates. If biological products are to be electrodialysed (serum) it is useful to keep the whole apparatus 24 hours in horse serum or other protein solution (hemoglobin) instead of water. The protein "coats" the membranes and transforms them from negative membranes into amphoteric membranes. (Very old and dried membranes cannot be coated readily in this way.)

If the membranes must be changed, the glass part of the apparatus is put in a sulphuric acid-bichromate solution and is ready for use after one or two days. The apparatus can be prepared in any size up to 100 mm. diameter, which, if the membrane distance is 80-100 mm., corresponds to 600-700 c.c. content.

The only disadvantage of the apparatus may be the large electro-osmotic effect sometimes seen, due to the filter plates, viz. thickness of the membranes. This may lead to a water movement, which usually occurs from the anode to the cathode, the membranes usually being negatively charged. Migration of the acid into the middle chamber can be avoided by increasing the rate of water circulation. If the membranes have different charges, owing to the difference of hydrogen ion concentration around or in the membrane, the water-flow into the middle chamber may be less or more than the outflow, which may lead to a dilution or concentration of the fluid in the middle chamber. In practice only the latter has been observed, which is usually desirable.

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OBSERVATIONS ON THE MECHANISM OF FORMATION OF COLLOIDAL SILVER*

BY HELEN QUINCY WOODARD

The earliest theory of the formation of colloidal metals by the Bredig[1] method postulated a simple thermomechanical process of evaporation of the metal in the arc, and subsequent condensation of the vapor to particles of colloidal size in the surrounding fluid. The work of Beans and Eastlack[2] and of subsequent workers in Beans' laboratory[3,4,5,6,7], showed this explanation to be inadequate, and established the formation of a gold-anion "complex" as necessary to the formation of colloidal gold. The work of Pennycuick[8] on colloidal platinum and of Eirich and Pauli[9] on colloidal gold shows that in the preparation of Bredig sols of these metals complex acids are formed through the action of the electric arc. In the present paper evidence is presented to show that the formation of colloidal silver by the Bredig method involves the reaction of silver with the electrolyte present according to the ordinary laws of physical chemistry simultaneously with the formation of a metal-anion "complex". No assumptions are made as to the nature of this "complex".

Apparatus and Materials

These were the same as those reported in previous papers[10,11].

Method

The sols were made, centrifuged, and analysed in the same manner as previously described[11]. pH determinations were made colorimetrically with suitable indicators to ±0.2 pH. Titrations for acid and alkali were made against N/100 NaOH or HCl, and were accurate to ± 7%. Thiocyanates were determined by titration against standard $AgNO_3$ to ± 2%. Sulfates were estimated to ± 10% by the turbidity produced with N/10 $Ba(NO_3)_2$. Nitrites were determined to ± 4% by titration at 35°C. against standard $KMnO_4$. Nitrates were estimated colorimetrically to ± 5% with diphenylamine reagent. Oxalates were estimated to ± 10% by titration against standard $KMnO_4$. (All precisions are given for determinations made on 3 cc. of .0015N reagent. Where the concentration was less the precision fell accordingly).

Results

As explained in a previous paper, when an arc is maintained between silver electrodes in a suitable solution, colloidal silver is formed, increases to a maximum of concentration as arcing continues, and then, upon further arcing, falls to zero. Table I gives the results of examination of the liquid

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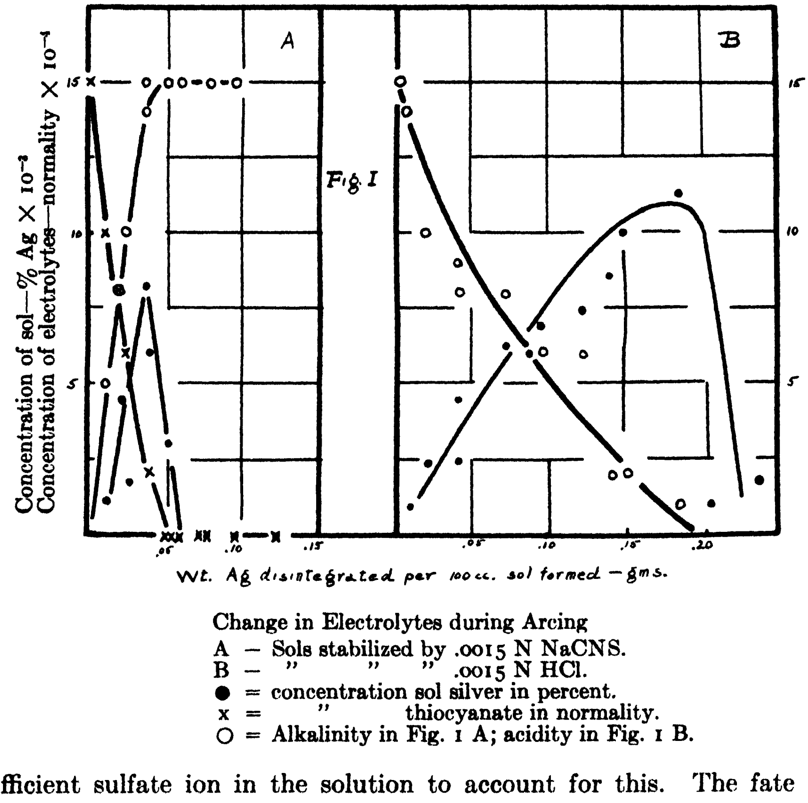
* From the Huntington Fund for Cancer Research, Memorial Hospital, New York City.

remaining after this final precipitation of the sol. The fate of the cation of the initial solution was followed by titration or pH determinations. Direct tests were made for some of the anions. Other anions were not determined directly, but are reported as silver salts because of the recovery of dissolved silver in sufficient amount to satisfy the anion originally present. Sol formation is reported as "+" when stable sols were formed regularly; "++" when the sols formed were concentrated and stable over a long arcing time; "−" when sols were never formed; and " ±" when the sols formed were extremely dilute, unstable on standing, or very sensitive to slight changes of technique.

An examination of the table suggests the following theory of sol formation:—In nearly all cases when arcing takes place in distilled water or in an electrolyte solution, silver reacts with the water sufficiently to saturate the solution with AgOH. This is shown by the fact that, except in certain special cases, the liquid remaining after a sol has been arced to precipitation has a silver concentration of .0002N − .0003N, and a pH of about 9.5. Two other processes take place at the same time. During arcing in a suitable electrolyte solution, a sol forms and precipitates according to the "complex" theory. In addition, silver combines with the anion present to form a silver salt. If the silver salt is highly insoluble, as AgCNS, AgCl, or Ag_2S, then the available anion is removed so fast from the solution that little can be used to stabilize the sol, and the sol is dilute. Qualitative evidence in favor of this hypothesis is furnished by the presence of a white deposit, presumably silver salt, in the sludge thrown down when sols prepared in NaCNS and NaCl solutions are centrifuged. If the silver salt is sparingly soluble, as Ag_2CO_3 or Ag_2CrO_4, then the anion is removed slowly from the system, and is available in considerable concentration long enough to stabilize concentrated sols. (Data for silver sols stabilized by K_2CrO_4 are not given in the table because the chromate ion is so good a stabilizing agent for colloidal silver that very prolonged arcing was necessary to precipitate the sols. This rendered quantitative work impossible). If the silver salt is moderately to highly soluble, as $AgNO_3$, CH_3COOAg, or Ag_2SO_4, then the disintegrated silver reacts with the electrolyte instead of dispersing, and no sol, or an exceedingly dilute sol, is formed. In this case the anion remains approximately constant in concentration during arcing (NO_3^-), or decreases slowly ($SO_4^{=}$). The decrease is probably due to adsorption on the sludge. This is evidently an electrolytic process, since only minute traces of silver (.00004N) are dissolved when the electrodes are left in contact with the arcing solution with the current not flowing.

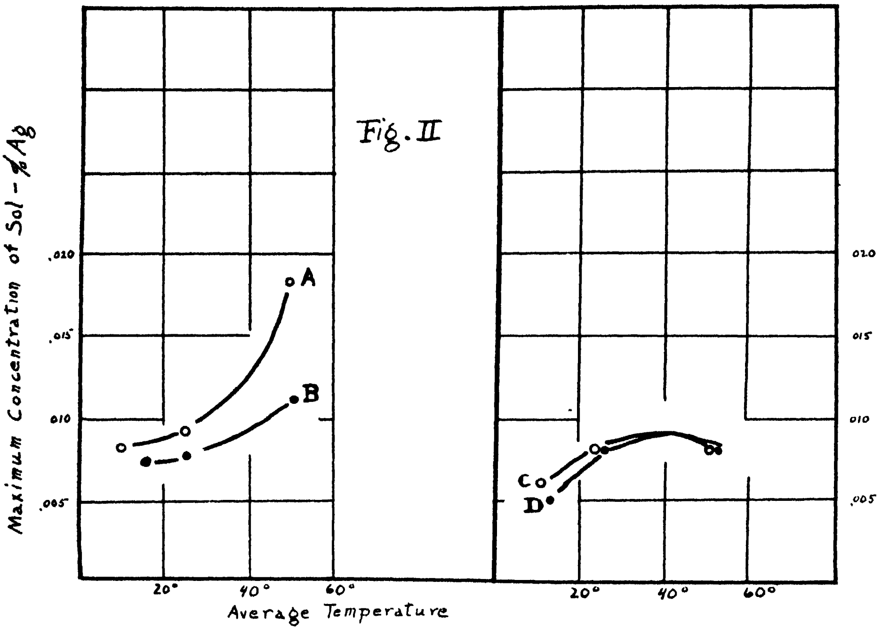
Interesting results are obtained when arcing takes place in the solution of an electrolyte whose anion is capable of forming a highly soluble silver salt. When the electrolyte is an acid, as H_2SO_4 or CH_3COOH, silver salt forms. The final solution is slightly alkaline, and contains sufficient silver to neutralize the acid and to saturate the solution with AgOH. When the electrolyte is an ammonium salt, replacement takes place, the silver goes into solution as silver salt, and the ammonium appears as hydroxide (NH_4NO_3 and $(NH_4)_2SO_4$). This is in contrast to the condition when arcing takes place in solutions of $NaNO_3$ or Na_2SO_4. Here the silver can not replace the sodium as it does the ammonium, and only dissolves sufficiently to saturate the solution with AgOH.

As the anion is removed from the solution as salt or precipitated "complex", the cation is set free to form hydroxide almost wholly (KOH, NaOH, NaCNS, Na_2CO_3, NH_4Cl, NaCl, NH_4NO_3, $(NH_4)_2SO_4$, $K_2C_2O_4$, CH_3COONa), or in part (Na_2SO_4, Na_2S). The sodium from Na_2SO_4 which is not recovered as hydroxide apparently remains in the solution as $NaHSO_4$, since there is sufficient sulfate ion in the solution to account for this. The fate of the portion of the sodium from Na_2S which is not recovered as hydroxide remains unexplained, although it might possibly be accounted for by preferential adsorption of NaHS on the sludge. If the electrolyte in the initial solution is an acid, the released H^+ disappears as H_2O (HCl, H_2SO_4, CH_3COOH).



Change in Electrolytes during Arcing
A – Sols stabilized by .0015 N NaCNS.
B – " " " .0015 N HCl.
● = concentration sol silver in percent.
x = " thiocyanate in normality.
○ = Alkalinity in Fig. 1 A; acidity in Fig. 1 B.

This process was followed directly with two electrolytes, NaCNS and HCl. Samples were withdrawn at intervals during sol formation. The samples stabilized by NaCNS were precipitated by solid $NaNO_3$, centrifuged, and the thiocyanate in the supernatant liquid was determined. The samples stabilized by HCl were titrated against N/100 KOH, the sols being diluted sufficiently so that a fair end-point was obtained. As no other acid was present, this gave a good indication of the concentration of HCl in the sol. A few direct determinations of the chloride content of the supernatant liquid remaining after the precipitation of these samples with $NaNO_3$ were also made. These checked the results of direct titration within the limits of experimental error. The results are given in Fig. I. It will be seen that the anion of the original solution disappears at about the same time as the precipitation of the sol in each case, while the alkalinity of the solution reaches its maximum at about the same point. This confirms the findings of Shear[5], Amsden[7], and Eirich and Pauli[9] for colloidal gold.



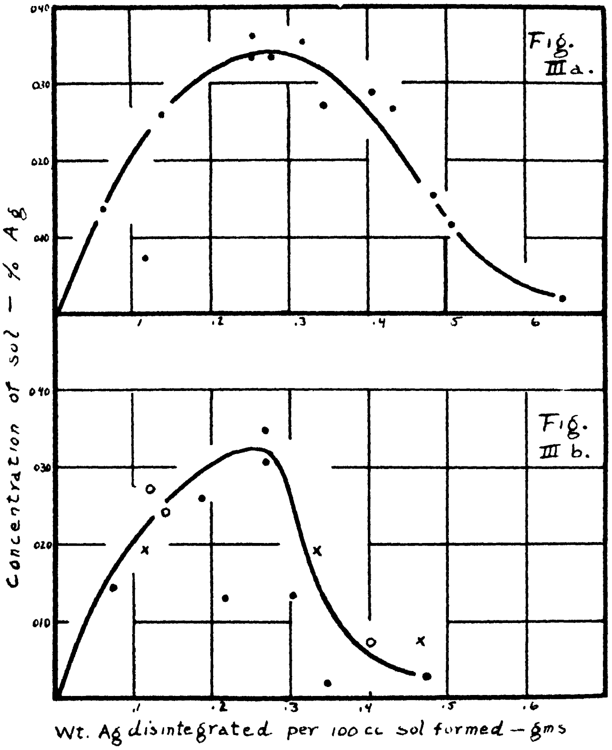
Change of Maximum Concentration of Sols with Temperature.

A = sols stablized by .0015 N NaCNS.
B = ” ” ” .0015 N HCl.
C = ” ” ” .0015 N H_2SO_4.
D = ” ” ” .0015 N CH_3COONa.

As the solubility of most silver salts increases markedly with temperature, it was possible to make direct tests of the influence of the solubility of the salt which silver is capable of forming with the anion of the stabilizing electrolyte, as is shown in Fig. II. Silver sols were made at the temperature ranges 5°—15°C., 15°—35°C., and 40°—60°C., in H_2SO_4 and CH_3COONa, and in NaCNS and HCl. The first two yielded anions whose silver salts are above the most favorable solubility for sol formation; the silver salts with the anions of the second two electrolytes are below the most favorable solubility for sol formation. In Fig. II the maximum concentrations of the sols formed are plotted against the average temperature. Two effects are evident in the curves. Rise of temperature in itself evidently favors sol formation, as is shown by the initial rise in all the curves. The favorable effect of rise in temperature is largely offset by the increasing solubility of the highly soluble

Ag_2SO_4 and CH_3COOAg. On the other hand, the increase in the low solubility of AgCNS and AgCl causes a marked rise in the curves for sols stabilized by NaCNS and HCl. The difficulty of maintaining an arc below 5°C. or above 60°C. rendered it impossible to follow these curves further.

Several points in the data remain unexplained by the theory presented above. The most important of these relates to the behavior of silver sols stabilized by KOH and NaOH. The alkalinity of these sols remains nearly constant during arcing and after the precipitation of the sol. If the cation is released during arcing and reforms the hydroxide as fast as released, then the electrolyte remains essentially unchanged. There is thus a constant supply of hydroxyl ion available for sol stabilization. One would therefore expect that the concentration of sol silver would remain constant at its maximum even after prolonged arcing. This is not the case, however, since silver sols stabilized by KOH or NaOH may readily be arced to precipitation. Further, KOH is formed during arcing in solutions of $K_2C_2O_4$, and NaOH



Figs IIIa and IIIb
Successive Sols made in the same Solution

a = first sols stabilized by .0015 N NaOH.
b = second sols stabilized by .0015 N NaOH
● = sols in NaOH remaining after arcing in .0015 N NaOH.
○ = sols in NaOH remaining after arcing in .0015 N NaCl.
x = sols in NaOH remaining after arcing in .0015 N Na_2CO_3.

TABLE I

Initial Electrolyte	Sol Formed	Cation recovered in final liquid	Anion recovered in final liquid	Final Ag conc.
.0009 N Na_2CO_3	++	100% as alkali	Trace	.0003 N
.0015 N "	++	100% "	"	.0002 N
.00075 N Na_2S*	+	45% as alkali		.0001 N
.0012 N "	+	50% "	0	.0001 N
.0025 N "	+	55% "		.0001 N
.00086 N KOH	++	100% as alkali	100% as alkali	.0003 N
.0013 N "	++	100% "	100% "	
.0009 N NaOH	++	100% "	100% "	.0002 N
.0015 N "	++	100% "	100% "	.0002 N
H_2O	−	pH 9.2		.0003 N
.0015 N NaCNS	+	70% as alkali	0	.0002 N
.0015 N HCl	+	pH 9.5	0	.0002 N
.0015 N NH_4Cl	+	80% as alkali	0	.0005 N
.0014 N NaCl	+	95—100% as alkali	0	.0001 N
.0005 N $NaNO_3$	±	pH 9.5		.0002 N
.0014 N "	±	pH 9.5	.0014 N	.0002 N
.0025 N "	±	pH 9.5		.0002 N
.0015 N NH_4NO_3	−	80% as alkali	.0014 N satisfied as $AgNO_3$	.0016 N
.0015 N $K_2C_2O_4$	±	100% as alkali	Rapid decrease during arcing	.0002 N
.0015 N $NaNO_2$	−	pH 9.5	Slow decrease during arcing	.0002 N
.0015 N CH_3COONa	+	100% as alkali		.0003 N
.0013 N CH_3COOH	−	pH 8.0	Satisfied as CH_3COOAg	.0018 N
.0015 N H_2SO_4	±	pH 7.2	Satisfied as Ag_2SO_4	.0017 N
.0015 N Na_2SO_4	±	50% as alkali	.0015 N	.0003 N
.0015 N $(NH_4)_2SO_4$	−	100% "	.0015 N satisfied as Ag_2SO_4	.0017 N

* Concentrations of Na_2S are given with respect to S content. Owing to hydrolysis, the Na content was about 20% higher. This is allowed for in calculating the percent of cation recovered.

remains in solutions of NaCNS, NaCl, and Na_2CO_3 from which the anions have been removed by sol formation and precipitation, yet prolonged arcing in these alkaline solutions does not result in the formation of sols stabilized by hydroxyl ion.

It seemed possible that the explanation of this anomaly lay in the presence of temporarily suspended sludge in the solution after the precipitation of the sol. This might provide nuclei for the condensation of metal vapor from further arcing, and so prevent the formation of stable colloid. That this explanation is correct is shown by the following experiment.

Sols were prepared in .0015 N NaOH, .0015 N NaCl, and .0015 N Na_2CO_3, and were arced to precipitation. The liquid remaining was then centrifuged to remove sludge. After centrifuging, the liquid was colorless, or retained a faint green color from traces of colloidal silver. This liquid was then used for the preparation of further sols. Sols so prepared were poorly reproducible, probably owing to the presence of traces of suspended silver. They had, however, approximately the same maximum of concentration and position of maximum as original sols made in .0015 N NaOH. This is shown in Fig. III. It was possible to repeat the process a third time with the liquid remaining after the precipitation of the second sols.

Further evidence in support of the above explanation was obtained by arcing to precipitation sols stabilized by .0015 N HCl. The liquid remaining after the precipitation of these sols only contained sufficient hydroxyl ion to bring the pH to 8.3—8.8, and no further sols could be formed in it even after prolonged arcing.

An observation which remains unexplained is that $K_2C_2O_4$ and $NaNO_2$ are not good stabilizing agents for colloidal silver, although their anions form salts with silver which are in the range of solubility favorable to sol formation. The theory in its present form is inadequate for these cases.

Summary

Evidence has been presented to show that the formation of colloidal silver by the Bredig method involves the effect of the laws of physical chemistry.

Bibliography

[1] Bredig: Z. angew. Chem., **11**, 951 (1898).
[2] Beans and Eastlack: J. Am. Chem. Soc., **37**, 2667 (1915).
[3] Beaver: Diss. Columbia (1921).
[4] Davidson: Diss., Columbia (1924).
[5] Shear: Diss., Columbia (1925).
[6] Layton: Diss., Columbia (1926).
[7] Amsden: Diss., Columbia (1926).
[8] Pennycuick: J. Chem. Soc., **1927**, 2600.
[9] Eirich and Pauli: Kolloidchem. Beihefte, **30**, 113 (1930).
[10] Woodard: J. Am. Chem. Soc., **50**, 1835 (1928).
[11] Woodard: J. Phys. Chem., **34**, 138 (1930).

THE REVERSIBILITY OF COUPLED REACTIONS IN BIOLOGICAL SYSTEMS AND THE SECOND LAW OF THERMODYNAMICS

BY DEAN BURK

The problem of the general applicability of the second law of thermodynamics to biological systems has of late years received attention of substantial character (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 13a). The two following different but hardly conflicting views summarize the present position. Lewis and Randall (8, p. 120) state, "The second law of thermodynamics is a principle which has never failed to satisfy the severest test of experiment." Donnan (12) states, as a result of probability calculations, "It seems, therefore, that there exist biological systems of such minute dimensions that the laws of classical thermodynamics are no longer applicable to them." It is the purpose of the present paper to offer some rather exact support for the first of these statements, without, however, detracting in any way from the suggestiveness of the second.

Both proof and disproof of the biological applicability of the second law, according to which no isothermal biological machine may spontaneously yield more free energy than it receives, have been difficult to establish experimentally in any particular instances. There is only one general class of biological reactions where, so far as experiment has been capable of deciding, it is certain that the second law is operating. This class may be designated as "the entire life processes of an organism." It has been universal experience that the thermodynamic work done by any organism has always been considerably less than the free energy consumed by that organism, i.e., in net effect heat has always been given to, and not taken from, the environment in amount greater than that minimum required by the second law. No perfectly reversible "whole life process" of an organism has ever been observed; the chemical free energy of the oxidizable organic matter supplied heterotrophic organisms or the radiant energy or oxidizable inorganic matter supplied autotrophic organisms has always been gradually, continuously, and often completely dissipated into heat.

The aforementioned class of biological reactions is, however, obviously extremely limited in number compared to the total number of biological reactions, when it is considered that the life process as a whole of any one organism is made up of an almost infinite number of more or less independent specific reactions. This opens the question of whether in some one or more of these specific reactions the law does not obtain but the infraction is not usually observed owing to the relatively overwhelming irreversible effects in the remaining specific reactions. The net reversibility of a life process as a whole is rarely greater than 50% and is generally only 10% or less, hence the free energy efficiency of any particular specific reaction under investigation has always been to a certain extent considerably obscured by the free energy losses in other simultaneous independent life processes. It has not been easy to exclude the frictional, and other irreversible, similarly irrelevant losses consequent upon life processes from the free energy balance sheets, so that only empirical "machine" efficiencies have been measurable, rather than what may be termed "second law" efficiencies.* The best review of the data concerning such machine efficiencies has been given by Baas-Becking and Parks (11) for the autotrophic processes whereby CO_2 is reduced by living forms by means of chemical energy supplied by the oxidation of sulfur, ammonia, carbon monoxide, hydrogen, etc. Machine free energy efficiencies give serviceable information regarding the fraction of useful work (i.e., CO_2 reduction) obtained in one process intricably and necessarily bound to many other useful chemical processes (i.e., growth, maintenance, etc.) which also consume free energy reversibly or irreversibly, as the case may be. Unfortunately they give no indication as to the degree of irreversibility of the isolated process itself, and can not, therefore, be employed as a test of the second law with respect to the isolated process (as has upon occasion been assumed) but only with respect to all life processes as a whole. The necessity for experimental, as distinguished from *a priori*, proof of the validity of the law has always been clearly recognized, particularly by its early formulators

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*The machine free energy efficiency is defined by the writer as the work done in any specific reaction occurring in a biological system divided by the free energy consumed by the system as a whole. The second law free energy efficiency is defined as the efficiency obtained upon correcting the machine free energy efficiency for the irrelevant losses involved in simultaneous extraneous metabolism (i. e., the work done in any specific reaction is divided by the free energy dissipated by that reaction only); specifically, it measures, in per cent, the real reversibility of an isolated reaction. Where reversibility is perfect and the second law operates, the efficiency attains one hundred per cent, but values higher than this may result in event that the second law does not obtain. When on the other hand, reversibility is not perfect (i. e., stoichiometric yields are not obtained, see nitrate reduction case), but where the second law operates, the efficiency is then less than one hundred per cent. In other words, there is one condition where the efficiency may be less than one hundred per cent, one condition where greater. The writer was for some time uncertain as to the nomenclature most suited to distinguishing the two efficiencies. Both efficiencies, as will be more evident upon consideration of specific cases, are "second law efficiencies" in the sense that they deal with relations of phenomena which take place in accordance with, or in exception to, the second law. The second law efficiency has been designed as a *test* of the law in cases where there might be considerable expectation as to the failure of its operation, and has been so named accordingly. In the case of the machine efficiency, on the other hand, more than one independent free energy consuming process is concerned, but only one is evaluated with respect to the free energy consumed in all processes and hence no test of the operation of the law in the one process is possible except in the unique event that the independent process so far disobeys the law as to more than cover the amounts of free energy disappearing in the other processes. But even here the quantitative extent of the disobeyal would be masked so long as the amounts thus disappearing in the other processes were unknown. The following contrasting terms have been considered as possible alternative nomenclature: (1) "machine efficiency" and "corrected machine efficiency"; (2) "overall efficiency" and "efficiency of isolated step"; or, in the case of autotrophic processes, (3) "efficiency as a machine for storing CO_2" and "efficiency as a machine for reducing CO_2". Each of these distinguishing designations has its objections, however. It is believed that the two terms finally chosen are fairly accurate descriptions of what they are intended to represent, especially when, as has been the case throughout this paper, an attempt has been made to point out that for the more fundamental applications of thermodynamics to life processes a great deal more is to be gained by isolating each process for consideration than by lumping together a number of generally chemically independent but physically inseparable processes. The proposed nomenclature therefore receives justification from its usefulness as an arbitrary convention based upon the proposed *principle of isolation* This isolation may amount to either a physical reality, or, more often, to merely a mathematical convenience.

(14, 15, 16, 16a*). In view of the historical interest attached to the various and almost solely theoretical discussions of the subject during the past hundred years, it has appeared desirable to present an experimental proof of applicability accurate to an order of about one per cent. This is now possible in a fundamental case (autotrophic hydrogen oxidation) involving a highly endothermic biochemical energy transfer process, only one important, but entirely probable, assumption obtaining.

Autotrophic Hydrogen Oxidation

We shall consider the non-photochemical reduction of carbon dioxide by the autotrophic hydrogen bacterium, *Bacillus pycnoticus*. This organism derives its energy from the oxidation of hydrogen. Its metabolism has been exhaustively investigated by Ruhland (17). Under the most favorable conditions only six and eight-tenths volumes of hydrogen are consumed for every volume of carbon dioxide finally changed to organic carbon. Calculations show that this ratio corresponds to a maximum machine free energy efficiency of $(105140 \times 100\%)/(54230 \times 6.8)$, or 28.4%, where 105140 and -54230 are the respective molal free energies of reduction of carbon dioxide and oxidation of hydrogen under the conditions of Ruhland's experiments (see below). However, such a machine free energy efficiency does not take into consideration the carbon dioxide reduced and then lost subsequently through respiration processes. Therefore, since it is not based upon the total carbon dioxide reduced, it can not be employed as a test of the second law with respect to autotrophic reduction of carbon dioxide by hydrogen.** The second law

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*Clausius (16a) says, "I can not but think that when it is asserted that heat never passes from a colder to a warmer body (however complicated the process) without some permanent change occurring which may be regarded as an equivalent thereof, this theorem ought not to be treated as self-evident."

**It will perhaps clarify matters further to illustrate the difference between the two efficiencies in the case of some purely non-biological system of energy transfers. Let us imagine a single motor arranged to perform simultaneously in an isothermal system a number of types of mechanical work, such as (a), moving a house, (b), sawing wood, (c), running a watch, etc., and that the amounts of work done in each case are respectively u, v, and w, and that the total mechanical work is $u + v + w = M$. Let the motor be driven by free energy supplied from a galvanic cell, and A be the total amount of free chemical energy lost as heat and work from the galvanic cell. We note that in the whole system there are five possible sources of irreversible production of heat, viz., m, n, o, p, and q, in respectively (a), (b), (c), in the running of the motor (d), and in the operation of the galvanic cell (e), the sum of the five heat losses being equal, let us say, to N, so that $A = (M + N)$. The machine free energy efficiencies in the cases of (a), (b), (c), (d), and (e) are then respectively u/A, v/A, w/A, $(u + m + v + n + w + o)/A$, and $(u + m + v + n + w + o + p)/A$; in each case the work done in any arbitrarily isolated process is divided by the work done and heat liberated in all five processes. The whole system, involving five processes (and therefore four energy transfers), is considered as a machine in which, in any one process, both the heat and the *work* used in the other processes before it and adjacent to it in the transfers are considered dissipated and unavailable with respect to the one process except the actual work done in that process. The corresponding second law free energy efficiencies are $u/(A - v - n - w - o - p - q) = u/(u + m)$, $v/(A - u - m - w - o - p - q) = v/(v + n)$, $w/(A - v - n - u - m - p - q) = w/(w + o)$, $(u + m + v + n + w + o)/(A - q) = (M + N - p - q)/(M + N - q)$, and $(u + m + v + n + w + o + p)/(A) = (M + N - q)/(M + N)$; in each case the work done in any arbitrarily isolated process is divided by the work done and heat liberated only in that *same* process, i. e., here the denominators are not all the same, but are all different. Comparing, in any one process, such as (a), the machine efficiency u/A with the second law efficiency $u/(u + m)$, it can be

(*Footnote continued on next page*)

efficiency may, and probably ordinarily should, be independent of the observed ratio of hydrogen to carbon dioxide used, variations in the ratio depending upon the relative amounts of respiration to organic carbon formed, i.e., upon the amount of energy expended to produce a given dry weight of organism.

Fortunately, in addition to measuring the hydrogen and carbon dioxide changes, Ruhland determined the oxygen consumption. The oxygen consumption provides a measure of the metabolic energy. Owing to this opportune circumstance, it is possible to determine the "second law" (as distinguished from the "machine") free energy efficiency and thereby test the law with respect to CO_2 reduction.

Ruhland gives eleven experiments with complete and unambiguous data concerning hydrogen and oxygen consumed and organic carbon produced, Nos. 2, 3, 4, 15, 19, 22, 28, 29, 30, 31, 32, as shown in Table I. Cultures of the organisms were grown at constant volume in approximately half liter, mercury sealed, flasks containing fifty cc. of mineral nutrient solution free from organic matter. Ammonium salts were employed as a source of fixed nitrogen. After gas evacuation the culture flasks were filled with varying amounts of oxygen, hydrogen, carbon dioxide and nitrogen, and immersed in a constant temperature bath at 32°C. Gas analyses were made at the beginning and at the end of the experiments. These usually lasted about ten days. Organic carbon was determined by wet combustion.

When the organisms are supplied suitable organic compounds of carbon no hydrogen is consumed.[1] On this account and others[1] it may be concluded that the process of carbon dioxide reduction and hydrogen oxidation can not be dissociated and that no reaction between hydrogen and ordinary[2] oxygen to form water takes place directly,[3] and that a high order of reversibility

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** *Footnote (continued from page 434)*

seen why the former is no test of the law as applied to the process (a), since A contains a great many terms in addition to, and obscuring, (u + m); only so far as (a) may disobey the law in such a manner that $u > A$ would the disobeyal be detected, and then, only qualitatively. We may note also the arbitrary nature of the principle of isolation, that, just as the system as a whole (described above) can be divided into various processes, so each of these processes might be divided into sub-processes of energy transfer more or less indefinitely; thus in (c), for example, we might isolate and determine the second law free energy efficiency of the transfer of the free energy of the motor to the stem of the watch, and then from the stem to the mainspring, and then from the mainspring to the minute hand, and then from the minute hand to the air currents set in motion, and so on. In the case of hydrogen bacteria, it may be considered that the free energy available in hydrogen oxidation, corresponding, let us say, to the free energy given to the motor above by the galvanic cell, is transferred, in effect, into (1) storing reduced CO_2 (corresponding to the u + m terms) and into (2) heat by reacting directly or indirectly with oxygen (corresponding to the p term), but to no other process (i. e., there are no corresponding v, n, w, or o terms); we shall be interested in distinguishing chiefly between the machine efficiency $u/(u + m + p)$ and the second law efficiency $u/(u + m)$. Here the number of terms is small, and all terms are experimentally measurable with but little uncertainty; in other biological cases, as will be shown, a greater number of terms (corresponding to v, n, w, o, etc.) are often involved and generally are difficult if not impossible to measure experimentally, and it is for this reason that it is so difficult to prove or disprove the application of the second law to the overwhelming majority of biological processes.

(*Footnotes 1, 2, and 3 on next page*)

probably obtains. All the hydrogen consumed being used to reduce carbon dioxide, all the oxygen consumed is therefore used in respiration, i.e., in metabolism, and oxygen consumption is a measure of metabolic energy. Oxygen consumption measures that fraction of the H_2 used for reducing the CO_2 which is later reoxidized back to CO_2 in the metabolic processes of the

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(*Footnotes for page 435*)

[1] Ruhland neither gives data nor mentions a single experiment showing hydrogen consumption to take place under heterotrophic conditions otherwise favorable for hydrogen consumption. However, he describes some dozen or more experiments wherein organisms were maintained heterotrophically in the presence of H_2 in .5% and 1% glucose with and without $CaCO_3$ or $MgCO_3$ without showing a trace of H_2 consumption although growth took place. In the cases without $CaCO_3$ or $MgCO_3$ the pH sank from 7.4 to 6.1 in 3 days and to 4.8 in 5 days. Ruhland was inclined to believe that this change in hydrogen ion concentration accounted for the lack of hydrogen consumption (in spite of growth occurring), yet his own data show that even in short time autotrophic experiments where the pH was initially low relatively large amounts of H_2 were consumed (many times the maximum experimental error of about .5 cc.), as reported in Table II. The experiments of Table II show that a certain amount of H_2 oxidation might have been expected in the heterotrophic experiments without $CaCO_3$ or $MgCO_3$ (taking place *at least* during the time that the pH was not inhibitory but only becoming so, which required about four days), provided that any H_2 could have been consumed at all. The experiments with $CaCO_3$ and $MgCO_3$, where presumably the pH was maintained constant at a favorable value, about 7.0, would seem to show conclusively, however, that no H_2 and CO_2 consumption takes place under truly heterotrophic conditions. A number of other experimental facts confirm this view. (1) The addition of sugar to an autotrophic culture actively and rapidly consuming H_2 (which was easily accomplished in Ruhland's apparatus without disturbing the gas mixture therein except momentarily) immediately stopped H_2 consumption but the oxygen consumption proceeded at practically the same rate (as shown by the behaviour of the manometer attached to the apparatus). (2) Mannite was observed to have the same effect as glucose. (3) In the system $H_2 + CO + O_2$, no CO is reduced by H_2, indicating that CO_2 must be reduced in order for H_2 to react. (4) Formate is not used as a source of carbon in the absence of H_2 or other organic matter, and yet H_2 may be used in its presence (CO_2 being present also), indicating that H_2 oxidation is resorted to only when a source of *sufficiently available* reduced carbon is not at hand. (5) Even H_2-consumption in the presence of sugar (and CO_2) under certain circumstances would not necessarily mean direct reaction with oxygen. In the case of normal inhibition of H_2- consumption there obviously must nevertheless be a certain low concentration of sugar which is not sufficient to completely inhibit H_2-consumption, and it is conceivable that the normal completely inhibiting concentration (i. e., about .5% at most) may not, under certain circumstances, be entirely effective. From any or all of these numerous reasons it appears to be reasonably safe to conclude that hydrogen never reacts to a measurable extent directly with ordinary oxygen.

[2] The designation "ordinary" oxygen is used to distinguish it from oxygen which might appear in such an equation as $CO_2 + H_2O \rightleftarrows CH_2O + O_2'$, where O_2' is *not* in equilibrium with the ordinary oxygen supplied in the reaction chamber but is activated in the sense that hydrogen may react with it. It actually may be a gas, or a peroxide form, etc., hydrogen acting as an oxygen accepter.

[3] Cultures of washed heavy cell suspensions of the organisms in a medium from which carbon dioxide and carbonate were excluded yielded a ratio of hydrogen to oxygen consumed of less than 2, about 1.8, but this can throw no light on the possibility of the direct water reaction taking place since a respiratory quotient of carbon dioxide to oxygen of less than 1 under these conditions could account for the result. Under such conditions of carbon dioxide—and therefore carbohydrate compound—starvation, a value of less than 1 is quite possible since bacterial proteins, and possibly to a very small extent fats, would be attacked, no compounds of the nature of organic acids being present, as Ruhland showed. Another explanation of the low $H_2:O_2$ ratio might be that the CO_2 derived from such respiration could then have been reduced again by the hydrogen, but not entirely, because of a partially efficient CO_2-absorbing alkali cup suspended in the reaction chamber which would have tended to remove some of the CO_2. With a respiration coefficient of 1, the observed ratio of $H_2:O_2$ of 1.8 would be accounted for if one eighth of the respired CO_2 was absorbed in the alkali, whereas if the respiration coefficient were less than 1, as suggested, alkali-absorption of even more than one eighth of the respired CO_2 could still leave the $H_2:O_2$ ratio of 1.8 accounted for. Using the Warburg apparatus Ruhland showed in fact that in the absence of H_2, CO_2, and HCO_3, but in the presence of O_2, large amounts of CO_2 were respired, the organic material being derived from the bodies of the organism themselves; in one experiment lasting only 5 hours, 6.4 mg. of bacterial dry matter gave off 2.1 mg. of CO_2.

organism. The remaining H_2 is a measure of the H_2 required to reduce the CO_2 to organic C found in the cells at the end of the experiment (Table I, Column 3). We see from Table I, Column 7 that this latter ratio, $(H_2-2O_2)/2CO_2$, is $(1169.22-(2\times 455.21))/(2\times 134.02)$, or .966 ± .012.* The probable error has been calculated by means of the usual formula $P.\ E = (.6745\sqrt{\Sigma d/n})/\sqrt{n-1}$ on the ratios $(H_2-2O_2)/2CO_2$ obtained from each of the eleven individual experiments, without, however, making a slight additive correction of several per cent for the fact that only eleven experiments are involved. This ratio is to be compared with the theoretical free energy efficiency ratio calculated from thermodynamic data, and then yields a measure of the second law efficiency and reversibility of the reaction.

Fortunately the thermodynamic data for the involved coupled reactions in their standard states is of the highest order of accuracy, owing, no doubt, to the general importance of the reactions. The coupled reaction in the standard state

$$2H_2(g) + CO_2(g) = 1/6\ C_6H_{12}O_6(s) + H_2O\ (l) \qquad (1)$$

$$\Delta F^\circ = 1184 \qquad (2)$$

may be divided into its two components and the actual states of the reacting substances indicated.

$$2H_2(.35\text{ atm}) + O_2(.06\text{ atm}) = 2H_2O\ (l) \qquad (3)$$

$$\begin{aligned}\Delta F &= \Delta F^\circ - RT\ln(.35)^2 - RT\ln(.06) - RT\Delta N\\ &= (2\times -56560) + 1250 + 1630 + 1780 = -108460 \qquad (4)\end{aligned}$$

where $\Delta F^\circ = (2\times -56560)$; $RT\Delta N$ is a factor correcting for the circumstance that the reaction takes place at constant volume (i.e., without external work), N being the mol volume change, in this instance -3; and the stated pressures of the gases are the averages between the initial and final pressures in each of the eleven experiments.

$$CO_2(.06\text{ atm}) + H_2O\ (l) = 1/6\ C_6H_{12}O_6(10^{-6}M) + O_2(.06\text{ atm}) \qquad (5)$$

$$\begin{aligned}\Delta F &= \Delta F^\circ - RT\ln(.06) + RT\ln(.06) + RT\ln(10^{-6})^{1/6}\\ &= 114300 + 1630 - 1630 - 1365 = 112935 \qquad (6)\end{aligned}$$

where $\Delta F^\circ = 114300$, and the activity of glucose is considered to be that of about 1/1000 the average cell carbon in 50 cc. of medium (and the maximum solubility of glucose 5M), i.e., (1/1000) (10 cc. /2) (1/22400) (1000/50 cc.) (1/5 M) = ca. 10^{-6} M per $(C_6H_{12}O_6)$.

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*The same value might have been obtained in a more roundabout manner by dividing the total hydrogen consumption by twice the total carbon dioxide reduced as obtained from the observed reduction (as organic carbon) plus that amount corresponding to the loss through oxygen consumption. The latter amount is equal to the oxygen consumption multiplied by the factor of about 1.03 obtained from stoichiometric considerations. Other ratio arrangements of known quantities in the three equations (1), (3), and (5) also yield the same result. See also footnote p. 439.

However, from the experimental data, the empirical formula of the reduced CO_2 as in equation (5) is not $(C_6H_{12}O_6)$ but $(C_6H_{12x}O_6)$ where x is slightly less than unity, $(1169.2-(2\times455.21) - 134.02)/134.02$, or .931, i.e., (cc. H_2 actually consumed, minus cc. H_2 appearing as H_2O as a result of combining with the O_2 lost from the gas phase of the system, minus cc. H_2 appearing as H_2O as a result of combining with one half the O_2 in CO_2 as in equation (1))/(cc. H_2 theoretically combined with C as in glucose). This gives for the true free energy of reduction of CO_2, $.931 \times 112935 = 105140$. This assumption involving the method of deriving a conversion factor for obtaining the free energy of reduction of $C_6H_{.931\times12}O_6$ from $C_6H_{12}O_6$ is the most uncertain element in the second law efficiency calculation.* What is indicated literally is that equation 5 should read

$$CO_2(.06\text{ atm.}) + .931\ H_2O(l) = 1/6\ C_6H_{.931\times12}O\ (10^{-6}M) + 1.931/2\ O_2(.06\text{ atm.});\ \Delta F = 105140 \qquad (5^1)$$

i.e., that (100 × (1.000 − .931)), or 6.9%, less H_2O must be decomposed to yield the necessary H_2 to reduce the CO_2.

In accordance with Equation 4 the oxidation of 2 mols of H_2 can furnish 108460 cal. of free energy. In accordance with Equation 5^1 the reduction of one mol of CO_2 requires a slightly smaller amount. Hence we should expect the following relation between the numbers of mols (or cc.) involved,

$$\frac{\text{(No. of mols } H_2 \text{ needed)}}{2\times\text{(No. of mols } CO_2 \text{ reduced)}} = \frac{105140}{108460} = .970$$

On the other hand, as has been shown, in accordance with Table I Column 7, the experiments gave

$$\frac{\text{(No. of mols of } H_2 \text{ used)}}{2\times\text{(No. of mols } CO_2 \text{ reduced)}} = .966 \pm .012$$

Hence there was apparently very slightly less hydrogen oxidized than was necessary to produce the available energy needed for the reduction of CO_2, the efficiency of the process being

$$100 \times \frac{.970 \pm .000}{.966 \pm .012} = 100.4 \pm 1.2\%,$$

if one assign a probable error (in distinction to any other type of error) of ± .000 to the thermodynamic data.

We see thus that (1) the reduction of carbon dioxide by hydrogen is a highly reversible, and if the figures be taken literally, perfectly reversible

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*Ruhland showed that no more than traces of fats or anaerobic carbohydrate decomposition products such as organic acids were detectable in culture of *B. pycnoticus* growing under autotrophic conditions. Burk and Lineweaver (18) have shown that the energy change from ammonia and glucose to bacterial protein involves only a small fraction of the combustion energy of the glucose, one to two per cent, ordinarily.

process,[*] and (2) the second law is not transgressed,[**] since the free energy efficiency is not significantly greater than 100%. The exact agreement can not, of course, be taken too literally, both on account of the experimental and probable errors involved in Ruhland's work and the thermodynamic calculations,[†] and the important assumption made that the free energy of reduction

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[*] By perfect reversibility is here meant the perfect reversibility of the isolated process of stored carbon dioxide reduction, and that *all* of the free energy of hydrogen oxidation concerned has been stored in the free energy of the stored reduced CO_2, rather than being converted irreversibly into a certain amount of heat. A certain amount of heat is of course given off in the isolated process since $\triangle F$ of Equation (3) is considerably smaller than $\triangle H$.

It is important to note that the ratio $(H_2 - 2O_2)/2CO_2$ gives no indication as to the possible extent of any direct reaction of hydrogen with ordinary oxygen; evidence on this point must be derived from other experimental sources (see footnote p. 436). The independence of this ratio from the amounts of hydrogen which might react directly with ordinary oxygen may be shown as follows:

Let us assume that the major reactions which accompany the life processes of the bacteria are

$$1.93\ H_2 + CO_2 = 1/6(C_6H_{.93x12}O_6) + H_2O \qquad (a)$$

$$1/6(C_6H_{.93x12}O_6) + 1.93/2\ O_2 = CO_2 + .93\ H_2O \qquad (b)$$

$$2H_2 + O_2 = 2H_2O \qquad (c)$$

Let x = no. cc. H_2 used in (a)
y = no. cc. reduced CO_2 used in (b)
z = no. cc. H_2 used in (c)

Then the total no. of cc. of H_2 used is $H_2 = x + z$

The total number of cc. O_2 used is $O_2 = \frac{1.93}{2} y + \frac{z}{2}$

The net no. of cc. of reduced CO_2 is $CO_2 = \frac{x}{1.93} - y$

Combining we obtain

$$\frac{(H_2 - 2O_2)}{2CO_2} = \frac{x + z - 1.93y - z}{2/1.93x - 2y} = \frac{x - 1.93\ y}{2/1.93\ x - 2y}$$

with the complete elimination of z, the number of cc. of H_2 reacting directly with ordinary O_2. The value of the fraction $(x - 1.93y)/(2\ x/1.93 - 2y)$ is, of course, by experiment .966, from thermodynamic data .970.

[**] It might be thought that perhaps the value of the ratio $(H_2 - 2O_2)/2CO_2$ is approximately unity merely as a necessary consequence of the major reactions that accompany the life of the bacteria. This is true, however, only so far as the second law *holds*. It is just this circumstance which permits the data to become a test of the law. Let us conceive of a case of transgression. If the organisms were able to make some such reaction as Equation 5, which requires a large amount of free energy, proceed spontaneously by means of heat energy taken from the surroundings in temperature equilibrium with themselves, they could then either store up free energy potentially as cell material or use the energy by recombustion. In the latter case no chemical change would be evident. In the former case, in addition to the chemical change involved in the cell material appearing, a certain amount of "ordinary" oxygen would have appeared which would not react with hydrogen. What the efficiency of 100% indicates is that the amount of CO_2 actually reduced is not greater than that permitted by the free energy of oxidation of hydrogen after all extraneous but perfectly clearcut losses of hydrogen (in this instance by indirect reaction with oxygen) have been accounted for. In other words, no reaction such as $CO_2 + H_2O = CH_2O + O_2$ has taken place spontaneously. Had it occurred the experimental ratio would have sunk below .966. We must conclude from the fact that the observed second law efficiency is 100% either that (1) the second law is not transgressed, or that (2) another chemical reaction (in the case under discussion one involving hydrogen) occurs in such a manner as to be exactly compensating with respect to both sign and magnitude. The latter possibility, which would involve reduction by hydrogen of the inorganic salts or the production of highly hydrogenated gaseous organic compounds, was not observed to take place.

[†] The free energy required in concentrating the salts from the culture medium into the cells would be negligible, calculations indicating that probably .1%, at most, of the free energy of CO_2-reduction would be involved, in such a direction, if at all, as to increase the efficiency from 100.4% to 100.5%. There are a number of other similar very minor factors involved such as changes in surface tension, pellicle formation, etc.

of carbon dioxide is exactly 105140 cals. per mol, whereas a value even two or three per cent different is conceivable. In any case, there can be no question but that the reaction is highly reversible and that an enormous difference obtains between the maximum machine efficiency and the second law efficiency, namely, a difference of between 28.4% and 100.4%. This difference, it may be stated again, is owing to the energy required to produce a given weight of dry matter (see Buchanan and Fulmer, 11a).

Table I

Ratio of Gases consumed by *Bacillus pycnoticus*. (From Ruhland).

Column Exp. No.	1 H_2	2 O_2	3 CO_2*	4 H_2/CO_2	5 H_2/O_2	6 $O_2:CO_2$	7 $(H_2-2O_2)/2CO_2$
2	137.82	52.75	16.90	8.15	2.63	3.12	.956
3	111.48	44.72	10 40	10.72	2.50	4.30	1.060
4	89.48	39.06	6 20	14.42	2.29	6.30	.916
15	87.92	41 15	3.00	29.31	2.14	13.7	.937
19	91.21	40 71	5.30	17.20	2.24	7.68	.924
22	103.20	39.39	13.10	7.88	2.62	3.01	.932
28	29.51	10.58	4.31	6.84	2.79	2.45	.969
29	85.20	30.64	10.89	7.84	2.78	2.82	1.098
30	113.13	40.71	17.01	6.65	2.78	2.39	.932
31	94.93	34.12	13.87	6.85	2.78	2.46	.962
32	225.34	81.38	33.04	6.83	2.78	2.46	.947
Total	1169.22	455.21	134.02				
Average	106.29	41.38	12.18	8.71	2.56	3.40	.966 ± 012
Relative	8.71	3.40	1				

* This refers to the C in the cells; i.e., reduced CO_2.

Indeed, an independent roughly quantitative demonstration of the operation of the second law might be based upon the dry matter requirement of *B. pycnoticus*. In the case of most bacteria and yeasts, etc., deriving their metabolic energy from respiration, three to six grams of glucose (or about 12000 to 24000 cals. of free energy) are required under the most favorable conditions to produce one gram of dry matter. The figures in Table I Column 6 show that these limits quite neatly cover the requirements of *B. pycnoticus*, which, of course, likewise obtains its energy of growth directly from respiration quite comparably to the bacteria and yeasts. In other words, since the machine efficiency is 29%, 29 + 71 cc. of reduced CO_2 are required to produce 29 cc. of stored reduced carbon dioxide, or 29 + 71 grams of sugar are required to produce approximately 29 grams of hydrogen bacteria, or a ratio of 3.4, which agrees with the best values derived from Column 6, where (O_2 :

CO_2) + CO_2 = 2.4 + 1 = 3.4, showing that the inefficiency of the bacteria considered as a machine for storing reduced CO_2 is entirely taken care of by its normal metabolic needs as judged by the needs of comparable organisms, and hence that the reversibility of the hydrogen-carbon dioxide reaction must be fairly high. Conforming to this view, the reason why the other known types of autotrophic bacteria all have much lower machine efficiencies (11, p. 104) is with little doubt owing to the fact that they also require much more energy to produce a given weight of dry matter.

It must be remembered in regard to the experimental data that the probable error of the mean, ± .012, is quite small in view of the facts that in the different experiments the H_2 consumed varied 8-fold (225 to 29 cc.); O_2 consumed 8-fold (81 to 10 cc.); organic carbon produced 11-fold (33 to 3 cc.); initial pH from 7.5 to 6.5; duration 11-fold (34 to 3 days); ratio of H_2 to O_2 used 2.79 to 2.14; ratio of H_2 used to CO_2 reduced 4-fold (29.1 to 6.6); and the rate of growth (final amount of organic matter produced per total time) 58-fold (5.2 to .09 cc. of organic C from CO_2 per day), as is shown for the most part by Table I. This shows that the wide variations in the ratio of total hydrogen to total carbon dioxide as given in Table I Column 4 are owing to variations in conditions of cell metabolism processes and not to variations in conditions of the efficiency or reversibility of the isolated coupled reaction of hydrogen oxidation—carbon dioxide reduction.

Attention should be drawn to the fact that the theoretical ratio based upon standard rather than actual free energies (as given in Equations 4 and 5[1]), uncorrected by the factor .931, is .990, not greatly different from .970; also to the fact that were the experimental ratio calculated from the five best experiments where the highest machine efficiencies were obtained (i.e., Nos. 28-32 where the ratio of H_2 to CO_2 was only about 7 to 8) it would be .968 ± .020, or little different from .966 ± .012 except for an increased probable error.

Finally, additional support for the second law is to be found in the opportune circumstance that the theoretical ratio is much smaller when based upon heats of reaction rather than upon free energies. The heats of reaction corresponding to Equations 3 and 5 are (2 × −68270) and 112300. Hence

$$\frac{(\text{No. of mols } H_2 \text{ needed})}{2 \times (\text{No. of mols } CO_2 \text{ reduced})} = \frac{112300 \times .931}{2 \times 68270} = .762.$$

In other words, if the entropy considerations of the second law be neglected, then, on the basis of heats of reaction, the biological machine could use (.970−.762)/.970, or 22% less cc. of H_2 per cc. of CO_2 consumed than calculated previously. We see, however, that the observed ratio is not significantly less than the minimum allowed by the second law, and hence the actuality of the latter's operation is somewhat strikingly indicated. Here is an interesting refutation of the Thomsen-Berthelot principle supplied by experimental observations on a living process rather than by *a priori* generalizations such as those of Guldberg and Waage, etc.

Summarizing,* we may say that it has been shown to within an accuracy of about 1% that (1) the second law of thermodynamics operates during the reduction of carbon dioxide by hydrogen,** granting the one assumption regarding the exact free energy of reduction of carbon dioxide, and (2) the reversibility is one hundred per cent (i.e., all the consumed H_2 reacts with CO_2 and none of the free energy of the isolated reaction is irreversibly converted into heat), granting further that the writer has given sufficient proof that the oxygen consumption is totally accounted for by respiration. There seems to be no reason to suppose that both the assumption in the first case and the proof in the second case do not hold rather exactly. In any event it is hardly conceivable that they are quantitatively inexact to such an extent as to affect the order of accuracy to more than a few per cent, possibly ten per cent,† rather than one per cent as stated. Even so, an experimental accuracy of to within 10% in the determination of the operation of the second law is far better than obtains in the cases of other known comparable coupled biological reactions involving large amounts of free energy.

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*It may be well now to briefly summarize the chief experimental data. (1) and (2), the hydrogen and carbon dioxide consumptions are known, which permit calculation of the machine free energy efficiency. (3), the oxygen consumption is known, which permits calculations of the second law free energy efficiency by correcting for the irrelevant losses of simultaneous extraneous metabolism. (4), hydrogen does not react with ordinary oxygen, which indicates high reversibility. (5), the difference between the machine and second law efficiency is confirmed as to order of magnitude by the probable free energy requirement of dry matter formation. In addition (6), it is to be observed that the chemical free energy of the hydrogen oxidation can be transferred consequentially only into either chemical free energy in reduced CO_2 compounds, or into heat.

**It is possibly an interesting observation that particularized proof of the second law for animate nature as given here is about a century less advanced temporally than particularized proof of the first law for inanimate nature. It is, of course, just one hundred years since Carnot first stated that the quantity of energy (motive power) in nature is invariable and *indestructible*, however much it may be changed from one form into another, and determined the mechanical equivalent of heat, some fifteen years before Sequin, Mayer and Joule. Although Rumford determined the mechanical equivalent of heat about 1798 to within twenty per cent of the correct value, he apparently did not correlate this with the idea of the *indestructibility* of energy, which is the essence of the first law as announced by Carnot, and a little later by Mayer, Grove, Helmholtz, Joule, Colding, and others. The equality, as distinguished from the proportionality (or some other function), between heat and work appears to have escaped conception and particularized proof until the later years of Carnot's life. Newton's Query 30 "Are not gross Bodies and Light convertible into one another?"can hardly be considered an anticipation of either of the laws of Conservation of Energy or of Mass, since neither the query nor the discussion following it imply a quantitative (as distinguished from a qualitative) convertibility, which, again, is the essence of these laws, just as by the Atomic Theory is meant Dalton's quantitative demonstration. Newton (Opticks, 2nd Ed., 1718, p. 373) unconsciously portrays the conception of the destructibility of energy maintained for centuries previous to the last one in his statements, "there is not always the same quantity of Motion in the World—Motion is always upon the Decay—if two equal Bodies meet directly *in vacuo* they will lose all their Motion (if elastic they will lose all but what they recover from their Elasticity) . . . .". While these clauses are possibly true, there is no implication that the lost motion is quantitatively converted into something else; it has been considered destroyed. For the same reason it can hardly be said that the Second Law is anticipated by the second very suggestive clause quoted, nor by the similar one (p. 375), "the variety of Motion in the World is always decreasing". Unusefulness is very different from total destruction. For an excellent historical review of work on the first and second laws between the years 1830-1880 see Planck "Das Princip der Erhaltung der Energie" (1921).

†See previous remarks concerning the energy requirement of growth. The growth energy must be derived from the reaction between oxygen and organic matter, i.e., from respiration, and it has been shown that in the case of *B. pycnoticus* the oxygen consumption no more than covers the approximate growth energy requirement, i.e., little or none is directly available for direct oxidation of hydrogen. See also footnote, page 436.

Autotrophic Methane Oxidation

The methane-oxidizing organisms are very similar to the hydrogen-oxidizing organisms, being facultatively heterotrophic and apparently yielding, under autotrophic conditions, fairly high machine free energy efficiencies as large as 30% (11). If the available data (17a) be taken literally the second law is not obeyed, however. In one experiment (in which the organisms were grown in an inorganic medium containing ammonium salts as a source of nitrogen and in an atmosphere of one part of methane to two parts of air), 225 cc. of methane and 148.7 cc. of oxygen were consumed, producing 99 cc. of CO_2 and an unmeasured amount of organic carbon, according to the equation:

$$225\ CH_4 + 148.7\ O_2 = 99\ CO_2 + 126\ CH_{2x}O_y + x'\ H_2O \qquad (10)$$

where x, x′, and y are unknown constants, $(x+x') = 225$, and the value 126 has been derived from $(225-99)$. Now 99 cc. CO_2 correspond to 99 cc. O_2, leaving only $(148.7-99)$ or 49.7 cc. O_2 to have formed both the water and organic matter. If no water were formed, the organic matter would have the formula (with respect to C, H, O, neglecting N, S, P etc.) $C_{126}H_{900}O_{99.4}$, or approximately $C_5H_{36}O_4$. If any water were formed the organic matter would still possess closely the same degree of reduction with respect to the valence of carbon. Such formulas, or degrees of reduction, while not experimentally disproven, are not only practically inconceivable, physiologically, but correspond to a second law efficiency of about 170%,[1] if it be assumed, as in the case of other bacteria, that the degree of reduction of carbon corresponds to glucose or thereabouts. Either the second law has really been transgressed or some unobserved reaction has taken place, probably a gaseous one involving H_2, N_2, CO, etc. The production of hydrogen gas, or its incorrect estimation as methane could entirely account for the discrepancy, not to mention, of course, sheer mistakes in determining oxygen and carbon dioxide or the undetected appearance of hydrocarbons such as C_2H_6, etc. The rather meager data on methane bacteria are discussed here not so much with respect to proof or disproof of the second law, but to show how, granting the applicability

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[1] Even considering no water formed in Equation (10) we have, after neglecting the respiration CO_2 formed which yielded only heat energy,

$$126\ CH_4 + 49.7\ O_2 + 26.6\ H_2O = 126\ CH_2O + 152.6\ H_2 \qquad (11)$$

In other words, some of the oxygen used to oxidize the methane to CH_2O is not atmospheric gaseous oxygen but must be considered as derived from bound oxygen, as in water, at no expense of energy and therefore contrary to the second law. Without troubling to distinguish between standard and actual free energies, Equation (11) may be split into two components

$$126\ CH_4 + 126\ O_2 = 126\ CH_2O + 126\ H_2O;\ \Delta F^\circ = (126 \times -80700) \qquad (12)$$

$$49.7\ O_2 + 152.6\ H_2O = 126\ O_2 + 152.6\ H_2;\ \Delta F^\circ = (152.6 \times 113120) \qquad (13)$$

yielding a second law free energy efficiency of $(152.6 \times 113120)/(126 \times 80700)$, or 170%. The increase of 70% over 100% is owing to the fact that $((152.6 \times 113120) - (126 \times 80700))/126$, or 56200 cal. of heat energy in the environment are employed contrary to the second law in changing a mol of CH_4 and H_2O to CH_2O and H_2.

of the latter, the second law efficiency calculations may be very useful in detecting impossible, improbable, or incomplete experimental biological data.[1]

In the only other experiment performed by Söhngen for which data are given, 161 cc. CH_4 and 193 cc. O_2 were consumed and 90.8 cc. of CO_2 were formed, yielding a second law efficiency very much less than one hundred per cent. Here, as may be shown, far too much oxygen is consumed, unless the organic material formed be assumed to correspond to an average degree of oxidation of practically HCOOH instead of CH_2O (even with no H_2 being produced), which circumstance, while not inconceivable, is most improbable. The machine efficiencies for both experiments were respectively 33.8 and 25.8% (11); yet, because they take no account of oxygen consumption, they give no inkling that (granting the second law) the data are incomplete as they stand, if not incorrect. This point is especially interesting when it is considered that the two experiments are unsatisfactory in opposite directions.

TABLE II

Effect of Initial pH upon Hydrogen Consumption (From Ruhland).

Exp. No.	Length of Exp. (days)	H_2 Consumed (cc.)	Initial pH
25	3	5.51	6.3
26	5	16.01	6.5
24	5	45.52	6.9
28	3	29.51	7.2
27a	4	35.49	—

The inaccuracy and extent of the experiments in the case of methane bacteria are not to be compared in any sense with those of hydrogen bacteria, and the poor data in the former case cast no reflection on those in the latter case. Consideration of the methane oxidation case has illustrated some common difficulties met with in attempting to apply the second law to any particular biological case.

Heterotrophic Nitrate Reduction

The non-photochemical reduction of nitrate to ammonia by the green alga Chlorella has been studied by Warburg and Negelein (19). In this case the energy is derived from the oxidation of carbohydrate, rather than from the oxidation of hydrogen. The free energy of the nitrate-ammonia reaction under Warburg and Negelein's experimental conditions

$$NO^-_3(0.1M) + H_2O\ (l) + 2H^+(0.01M) = NH^+_4(0.005M) + 2O_2(0.2\ atm) \quad (7)$$

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[1] The showing by the writer (13), for example, that the free energy of glycogen-lactic acid breakdown in muscle is considerably smaller than the theoretical maximum work of muscle as obtained by the tension length diagram area method has led, in part, to the discarding of this method of measurement of the theoretical maximum work, in favor of the heat liberated in relaxation.

is +68000 cal. (19). The energy relations are, interestingly enough, approximately the same as those obtaining in the case of the reduction of nitrogen to ammonia (i.e., nitrogen fixation) by carbohydrate, where the free energy required is +73800 (18).

The approximate maximum possible yield obtainable in the coupled nitrate reduction and carbohydrate oxidation reactions, employing Warburg's value for the free energy of combustion of glucose (−690000), calculates to be (690000/6)/68000, or a ratio of 1.69 mols of NH^+_4 per mol of CO_2 formed. The observed ratio (Table III, Protokolle 12, 13, 14) was, under *optimum* conditions, i.e., after about the third hour, .193 (Table III, Protokoll 13C), or a maximum machine free energy efficiency of ammonia production of .193/1.69, or 11.5%. Under infra-optimal conditions, i.e., during the first and second hours, the efficiency was also found to be zero independently of time under any conditions of high pH, i.e., greater than pH 2; no ammonia was produced by cells maintained in (a) 0.1 N $NaNO_3$, (b) 0.1 N Na_2SO_4 − 0.01 N H_2SO_4, (c) 0.1 N KH_2PO_4, or (d) Knop's solution containing nitrate (Table III, Protokolle 3, 4, 5, 6). In these latter solutions the respiration quotient was 1, within experimental error, although under conditions of ammonia formation the quotient ordinarily rises to about 1.7 (Table III, Column 5).

The efficiency thus calculated has included the energy represented by the CO_2 of normal metabolism as well as that involved in NH^+_4 formation, and is therefore the machine efficiency by definition. When the CO_2 of resting or normal metabolism (i.e., that amount given by the oxygen consumption since the normal respiration quotient is 1) is excluded, the maximum observed ratio of (mols NH^+_4)/(mols extra-CO_2) reached .532 (Table III, Protokoll 13C) corresponding to a maximum second law efficiency of ammonia production of .532/1.69, or 32%.* Here again the second law efficiency may decrease to zero under the same two conditions governing the decrease of the machine efficiency to zero.

Warburg and Negelein (19, Protokoll 7) show that the rate of oxygen consumption is increased about 40% during the first hour when the organisms are maintained in .1 N $NaNO_3$ − .01 N HNO_3 instead of in Knop's solution. Strictly speaking, this might mean that the maximum second law efficiency of about 32%, as calculated, should be about 48% less (i.e., $\frac{(.4 \times 100)}{(1.4 \times 1.6) - 1.4}$, where .4 is the relative increase in oxygen consumption, 1.4 is the relative total oxygen consumption, and 1.6 is the respiration quotient), were it not for the fact that the oxygen consumption rate decreases (see Table III,

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*The second law efficiency here calculated to be 32% was approximately that given by Warburg and Negelein (19, p. 383) and Meyerhof (20, p. 95). These workers did not calculate the machine efficiency (reaching a maximum of 11%), and failed to indicate that the efficiency they obtained was not to be compared with the efficiencies for autotrophic processes where, so far as the writer is aware, the efficiencies given in the literature have always been machine and not second law efficiencies. For example, the nitrate-ammonia second law efficiency of 32% is not to be compared with the machine efficiency of nitrification found by Meyerhof (20) to be 6%.

TABLE III

Data concerning Nitrate-Ammonia Reduction (from Warburg and Negelein).

Col. 1	2	3	4	5	6	7	8	9	10	11	12
Proto-koll	Expt.	Time (hr)	O_2 cmm. consumed	$\frac{CO_2}{O_2}$	Total CO_2 (cmm.)	Extra-CO_2 (cmm.)	NH_3 10^{-6} mols	Mols NH_3 to mols total CO_2	Mols NH_3 to mols extra-CO_2	Machine efficiency %	Second law efficiency %
12^v	a	1st	365	1 74	635	270	1 0	.0352	.0823	2.09	4.90
	b	2nd	293	1.81	530	240	3 0	.127	.280	7.55	16.6
	c	3rd 4th	258 241	1.63	815	320	6 0	.164	.420	9.8	25.0
13^v	a	1st	233	1.70	396	163	1.2	.0565	.165	3.36	9.82
	b	2nd	201	1 74	350	149	1.2	.0767	.180	4.56	10.7
	c	3rd	178	1.57	279	101	2 4	.193	.532	11.5	31.6
14^v	a	1st	253	1.62	409	156	0.9	.0493	.129	2.93	7.68
	b	2nd	226	1 62	365	139	1.3	.0798	.209	4.75	12.4
	c	3rd	201	1.43	288	87	1.8	.140	.464	8.34	27.6
3^w	a	1st	102	1.03	105	1	0	0	0	0	0
4^x	a	1st	102	1.04	106	0	0	0	0	0	0
5^y	a	1st & 2nd	65	1.03	67	2	0	0	0	0	0
6^z	a	1st & 2nd	38	1.00	38	0	0	0	0	0	0

[v] Low pH (i.e., 2) with nitrates (.1N $NaNO_3$ − .01N HNO_3).
[w] High pH (i.e., >2) with nitrates (.1N $NaNO_3$).
[x] Low pH without nitrates (.1N Na_2SO_4 − .01N H_2SO_4).
[y] High pH without nitrates (.1N KH_2PO_4).
[z] High pH with nitrates (Knop's solution).

Column 2) by the third hour (when the maximum efficiencies are obtained) to about normal so that the correction is probably unnecessary (but see later discussion). It is obvious that the second law is obeyed so far as ammonia production is concerned, since the second law efficiency is considerably less than 100%.*

It is practically impossible to derive any satisfactory proof of the second law in the case of nitrate reduction as a whole, as will now be shown. Too many assumptions would be involved, in the absence of experimental data. The chief difficulty lies in the fact that Warburg and Negelein give no data to show that the ammonia produced under optimum conditions of efficiency corresponds stoichiometrically with the nitrate disappearing (nor did they analyze the cells for increase in organic nitrogen). Such determinations would be very difficult to carry out, of course, since it would mean measuring decreases of roughly 10^{-5} to 10^{-6} mols out of 10^{-1} mols of nitrate per liter of

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* The writer would venture to suggest a means of predicting the probable maximum second law efficiencies to be expected in cases of isolated coupled reactions, making the assumption, of course, that the second law holds. In the case of nitrate reduction, we have, approximately,

$$H^+ + HNO_3 + H_2O = NH^+_4 + 2O_2;\ \triangle F = 68000$$
$$X\,O_2 + X\,CH_2O = X\,CO_2 + X\,H_2O;\ \triangle F = -X\,115000$$

where with perfect reversibility X would equal 68000/115000, or .59. It will be observed, however, that experimentally the mechanism proceeds corresponding to X equals at least 2, the least number of oxygen molecules in the equation requiring energy.

Similarly, in the case of hydrogen oxidation we have approximately,

$$CO_2 + .93\,H_2O = 1/6CH_{1.86}O + 1\,93/2\,O_2;\ \triangle F = 105140$$
$$X\,O_2 + 2X\,H_2 = 2X\,H_2O;\qquad \triangle F = -X\,108460$$

where the perfect reversibility X would equal 105140/108460 = 97 and again it will be observed that experimentally X actually equals at least .97, the least number of oxygen molecules in the equation requiring energy.

In other words, in both cases, the maximum amount of free energy-yielding reaction taking place is possibly determined not only by the amount of free energy demanded in the free energy-requiring process in accordance with the second law, but also by the stoichiometry of the latter. Expressed in more strictly chemical terms, *all* the incidental compound produced in the free energy-requiring reaction (in the above particular cases oxygen) must, by virtue of the mechanism chosen by the organism, be consumed in the free energy-yielding reaction.

This "biochemical reversibility principle" stands in much the same relation to the second law as the second law does to the first, namely, as conditioning the convertibility of energy from one form into another, and states that of the free energy available in the free energy-yielding reaction of a coupled reaction taking place in a biological system only a fraction of this is available under biological conditions, the loss of availability being determined by stoichiometric considerations. The greater the free energy of the free energy-requiring reaction in proportion to the free energy of the properly stoichiometric free energy-yielding reaction, the greater will be the maximum reversibility and second law efficiency, up to 100%. An analogous, but not in all respects similar principle is employed by Warburg in explaining the varying efficiencies of different wave lengths of visible light in the photosynthetic reduction of carbon dioxide, where $N_0h\nu$ grows proportionally to ν, while U, the energy required remains constant, so that the efficiency must vary with wave length. While the "biochemical reversibility principle" has been proposed upon the experimental basis of only two cases, it is to be observed that the two cases present widely different reversibilities (namely 32 and 100 per cent), which is in favor of the principle. It is not anticipated that invariable applicability will necessarily obtain. The word principle has been used in the sense of being a generalization of experience applying in a number of cases, in distinction to the word law, which is a relation of phenomena invariable under given conditions. Without going into detail it may be stated that according to this principle the reversibilities of isolated autotrophic reductions of carbon dioxide should approximate perfection, whereas the reversibilities of heterotrophic consumptions of organic carbon compounds should usually be fairly low i.e., 0 – 50%, and, so far as is known, this is the case.

solution. Without either this information or calorimetric measurements (see later) it is impossible to properly account for the (100 − 32%), or 68%, efficiency loss, i.e., to know whether the loss can be explained upon the basis of other reduction products (involving storage of chemical free energy) or heat evolution; we know the second law efficiency of ammonia production but not of nitrate reduction as a whole (i.e., reduction to ammonia and other nitrogenous compounds).

It was shown that normally no appreciable amount of ammonia is to be found inside the cells, and that NO, N_2, and NO_2 were not produced. The possibility of numerous other likely intermediate nitrogen compounds was, however, not experimentally excluded (i.e., by chemical analysis) and there can be no question that during the first hour or two of ammonia production part of the reduction products do not appear as ammonia but are built into the cell tissue (Table III, Protokolle 12, 13, 14), since it was shown that cells which had been previously starved for nitrate and then placed in nitrate solution at pH 2 gave high respiratory quotients of 1.7 etc., without, however, producing ammonia (19, Protokolle 16, 17). The total extra cellular ammonia nitrogen content never rose much above 5×10^{-6}M whereas the concentration of organic cell nitrogen in algal cultures may attain values one thousand times as great. Judging from this evidently small percentage of nitrogen appearing as ammonia, it is possible therefore that even under conditions of maximum observed efficiency there are nitrate-reduction products which do not appear as ammonia but disappear in assimilation, the observed concentrations of ammonia merely representing balances between ammonia production and assimilation. Now the aforementioned decrease in rate of oxygen consumption to normal by three hours might have occurred because the organisms were able to make some such reaction as Equation 7 take place spontaneously without any corresponding expenditure of energy upon their part; the oxygen given out by such a reaction would tend to lower the observed rate of oxygen consumption (the decrease might be owing, of course, to any number of factors, such as decreasing concentration of respirable carbohydrate, lowered vitality of the cells, etc.). It should be pointed out also that the oxygen consumption continues to decrease to values much below normal (19, Table 19). On account of the unknown reason for both the initial increase and the subsequent marked decrease in rate of oxygen consumption, it is therefore unfortunately true that until it can be shown that the nitrate disappearing corresponds stoichiometrically either with the ammonia appearing or other reduction products of nitrate the possibility exists that the second law does not operate in nitrate reduction as a whole.

Still another possible difficulty arises from the fact that no efficiency data are available for periods of time later than the third hour, at which period the efficiency is increasing at a marked rate; indeed not only the first differential but also the second differential of efficiency with respect to time is increasing (Table III, Protokolle 13 and 14, Column 12). It is true that the decrease in oxygen consumption after three hours may explain how the efficiency might increase after three hours, as it promises to do; i.e., after three hours the reaction may not take place according to

$$HNO_3+H_2O+2/6(C_6H_{12}O_6)=NH_4^+ +2CO_2-162000 \text{ cal. (heat, see below)} \quad (8)$$

Some of the oxygen may then appear as gas, causing the observed decrease in rate of oxygen consumption, rather than reacting with carbon in carbohydrate. This explanation involves a sudden change of mechanism at the point where a 32% second law efficiency is attained and is therefore improbable. Warburg and Negelein offer an explanation for the increase of oxygen consumption when the cells are placed in the nitrate mixture at pH 2, but they take no note of the difficulties offered by the subsequent decrease, nor the difficulties presented by the promised increased efficiency after the third hour. The possibilities that either (1) some of the extracellular ammonia after the third hour is derived from breakdown of cell organic nitrogen (i.e., ammonification) or (2) the carbon oxidized corresponds to a reduction stage considerably different from that in carbohydrate, do not seem very probable, but must also be taken into consideration.

It is to be observed that the uncertainty in regard to proof of the second law consequent upon not knowing the stoichiometric relations in the case of nitrate reduction does not obtain correspondingly in the case of carbon dioxide reduction by hydrogen. Here, even if it had been true that the reversibility was not 100% (i.e., that some hydrogen reacted directly rather than indirectly with oxygen to form water), the proof of the second law would have been in no way affected since all the reactants of the then irreversible reaction, hydrogen and oxygen, would have nevertheless been accounted for, having disappeared in the ratio 2:1 as in water (see also footnote p. 439).

A fair approximation to proof of the applicability of the second law might be obtained from calorimetric measurements, i.e., it might be possible to show that the difference between 32% and 100% could be accounted for entirely as heat, providing ammonia was the only nitrogenous reduction product of nitrate. According to Equation (8), all of the oxygen given out according to Equation (7) has reacted according to Equation (5) (taking place in the reverse direction however), and that of the approximately 230000 cal. available per $2O_2$ only 68000 cal. have been converted into chemical work, the rest, about 162000 cal., appearing as heat. The measurement of this 162000 cal. has not been carried out calorimetrically, as yet however.[1]

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[1] Meyerhof (20) performed a somewhat similar experiment in the case of autotrophic nitrification for the reaction $NO_2 + \frac{1}{2}O_2 = NO_3$. The machine efficiency as determined chemically was about 6%, and Meyerhof found as the average of a series of calorimetric experiments that the heat given off per mol of nitrate formed actually corresponded to about (100 − 6) or 94% of that given by the heat of reaction. Owing to the small efficiency yield, and the accuracy of calorimetric determinations in general, and, indeed, a number of other experimental uncertainties, this proof of the second law can not be considered very accurate, altho it is possibly as accurate as for any comparable coupled reaction case apart from autotrophic hydrogen oxidation. The calorimetric measurements in the nitrification case correspond to the oxygen consumption measurements in the hydrogen oxidation case; they determine directly or indirectly the metabolic energy. The nitrification case really presents a much better demonstration of the first law than the second, since all but approximately 5% of the chemical energy was converted into, and obtained as, heat, as required. Here it is not determining a quantity as a small difference between two large quantities, but rather comparing two large and nearly equal quantities.

Summarizing, we see that in the nitrate-ammonia reaction it is possible to calculate both the machine and second law free energy efficiencies (and therefore the reversibility and the applicability of the second law) as in the case of autotrophic hydrogen oxidation, but, owing to lack of certain data (i.e., data accounting for the difference between the maximum observed second law free energy efficiency and an efficiency of 100%), it is as yet impossible to test the applicability of the second law of thermodynamics to nitrate reduction as a whole. It has been found again that a large difference (about 3-fold) obtains between the two types of efficiencies. In other cases to be mentioned below such large differences will not always exist.

The Reversibility of Other Coupled Reactions

a. Partially Reversible Reactions

The non-reconversion of the potential energy of tension in isometric muscular contraction presents a case where the second law free energy is zero; where, so far as is known (see 13, p. 167) the process under anaerobic conditions is totally irreversible, all of the tension energy being converted into heat, rather than some being used to condense lactic acid back into a hexose, or into glycogen.

The anaerobic reconversion of lactic acid into glycogen is partially reversible, generally twice as much energy being consumed as required under ideal conditions, i.e., the second law efficiency is only about 50%. That is to say, when lactate is added to muscle in Ringer's solution, four to six molecules of lactate are reconverted per molecule of lactate burned to carbon dioxide, whereas according to the free energies involved about ten reconverted molecules are possible under perfectly reversible conditions.

The maximum second law free energy efficiency of aerobic muscular contraction (mechanical work done)/(chemical free energy consumed) is only about 15 to 25% (13), and according to the latest data of Hartree and Hill (25) the second law efficiency of anaerobic human arm muscle contraction reaches a maximum of about only fifty per cent, in the case of frog sartorius muscle contraction, thirty per cent. In the cases of the partially reversible reactions mentioned in this section, the machine efficiencies are practically as large as the second law efficiencies owing to the fact that the resting metabolism of the muscle is very small compared to the coupled reactions it carries out. This will also be true of other coupled reactions carried out by multicellular organisms, because the ordinary metabolic chemical energy liberated is much more organized and disciplined to subserve function. Brown (24) has shown, for example, that the "maintenance" metabolism of man is some 100 times as small as that of yeast per units of weight and time.

If the latest conclusion of Hartree and Hill (26) be accepted that the isometric relaxation heat represents the maximum mechanical work capable of being performed by a twitched frog sartorius muscle under anaerobic conditions, then the second law efficiency (mechanical work)/(mechanical work + relaxation heat when work is done) = (mechanical work)/(isometric relaxation heat) may apparently reach the high value of 71% (26, Table II). Even under tetanic conditions (i.e., where the stimulus is continued for some time, .2 to .4 of a second), the corresponding second law efficiency attains values approximating 50% (26, Table IV, (d)/(d+f)).

The main thermodynamic work which microorganisms perform is that of growth.* Brown (24) has shown that when yeast is maintained at a concentration sufficient to prevent reproduction, the heat given off per gram of maltose fermented is 125 cal., whereas when growth is allowed to take place only 8.5% less heat is given off, 114.4 cal. It is likely that relatively little of this 114.4 cal. is necessary for true maintenance energy, since similar yeast juice containing no intact cells would give about the same value. Brown's findings confirm the view that the breakdown of carbohydrates, etc., by unicellular microorganisms is often if not usually conditioned chiefly by the concentration and activity of the cell enzymes necessary therefor and the concentration of carbohydrate, independently of whether the organisms are able to take advantage of the energy liberated. Wasted heat, as illustrated in the work of Brown, is chiefly the result of uncontrolled enzymes acting on an appropriate substrate, the organisms possessing no mechanism, as do multicellular organisms, for closely regulating the amount of substrate in contact with cell enzymes, and correlating most of the energy liberated with some vital function requiring free energy. The free energy efficiency of growth obtained by Brown (about 8.5%), it may be mentioned, is somewhat less than maximum values usually reported for yeasts, fungi, bacteria, etc., where, as has already been pointed out in discussing the amount of sugar required to produce a given weight of dry matter, the maximum efficiencies vary from about 15 to 30%.

In all these partially reversible reactions just discussed the same kind of difficulties in the way of proving the second law with regard to the processes involving the energy not appearing as work in the primary process obtains as in the case of nitrate reduction—too many assumptions become involved in the absence of all the necessary experimental data, which, it may be added, is often difficult or impossible to obtain. There is generally at least one unknown too many. We see how every much more difficult it is to prove the second law in heterotrophic rather than in the less complicated autotrophic coupled reactions.*

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* Angerer (22) and Ludwig (23) have shown that an inconsequential fraction of the metabolic energy of motile microorganisms is accounted for by motility, in the neighborhood of 0.1 per cent. Considering the relative amounts of energy involved in motility and Brownian movement by a single microorganism one might doubt that, although some organisms may be able to disobey the second law by in some manner converting the heat energy of Brownian movement into work, the amount of work so accomplished and gained would be significantly appreciable.

b. Highly Reversible Reactions.

There are a number of reactions occurring in biological systems which are highly reversible: chemical equilibria such as reactions between (1) haemoglobin and oxygen, (2) haemoglobin and methaemoglobin, (3) the respiration enzyme and oxygen, (4) the respiration enzyme and carbon monoxide, (5) hermidin and cyanohermidin, (6) reduced and oxidized echinochrome, (7) ordinary and active glucose (21), (8) hydrogen ion buffer systems, (9) nitrogen gas and an initially fixed form (18), and (10) succinic acid and methylene blue to give fumaric acid and leuco-methylene blue. Most of these reactions take place under approximately equilibrium conditions** and their free energy changes are consequently practically zero. It is also true that a number (i.e., (1), (2), etc.) are not coupled reactions in the sense used in this paper, since they do not involve a free energy storing process but only a heat change; in the case of hydrogen oxidation, for example, if hydrogen reacts with carbon dioxide, free energy is stored as carbohydrate (etc.) produced, and the reaction is coupled, whereas if hydrogen reacts directly with oxygen and the energy is given off as heat, no free energy is stored, and the reaction is not considered as coupled. Chemical free energy is considered as "stored" when the chemical substance or substances formed are still out of practical equilibrium with the environment (in the bacterial case, oxygen, i.e., carbohydrate would be out of equilibrium with oxygen, water, however, practically in equilibrium with oxygen).

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* If one were to set out to look for cases where the second law might not be obeyed in biological systems the most likely field, *a priori*, would lie in reactions involving small amounts of free energy, i.e., carbohydrate and protein hydrolytic equilibria, etc. A small shift in position of the equilibrium point would require little energy but could result in a large chemical change relatively easily detected. The difficulty of excluding extraneous free energy reactions would be greater, of course. Donnan's statement quoted previously was made with reference to systems of dimensions of the order of 10^{-15} ccm., or less; so that in order to consider a series of such systems amounting to macroscopic dimensions, it requires one additional logical step to suppose that the infra-microscopic systems might all fluctuate together simultaneously in such a manner that the second law would no longer be applicable to the macroscopic system as a whole. This logical step would, indeed, be the real issue awaiting test, since, beyond question, if the size of any one system is made small enough the second law as classically stated by Clausius could not apply. The utilization of fluctuations in the organized, non-random, and extensive manner indicated is to be classed as true perpetual motion of the second kind, whereas the occasional fixation of random fluctuations of the type indicated by Donnan would not necessarily involve such an implication, since compensation would in the long run probably take place.

** Although one can conclude from the fact that when equilibrium conditions exist the reversibility is very high or practically perfect, it does not follow, or course, that the second law is necessarily operating, since the biological machine (i.e., the organisms) may have shifted the equilibrium point without corresponding expenditure of energy upon its part. So far as the writer knows, there are no cases as yet where it has been shown that the equilibrium point is the same both in and out of the biological system, at least with any desirable degree of accuracy.

The second law efficiency of the photosynthetic process in plants whereby CO_2 is reduced to sugar may attain fairly high values. Thus in the simplest case as studied by Warburg and his co-workers, where all the incident light energy is absorbed by the photosynthesizing machine (Chlorella) a maximum efficiency of about 60% is obtainable. An accounting for the remaining unutilized 40% of the energy as heat (or possibly, in part, as other chemical energy) has not been made and it is conceivable (so far as present experiments may decide), although not probable, that the second law is not observed in some other reaction occurring simultaneously with sugar formation and that heat is being absorbed from the environment in addition to the radiation absorbed and that required by the second law. If the photosynthesizing process be considered from the standpoint of mechanism to form glucose and hydrogen peroxide, first, and then later glucose and oxygen, the second law efficiency of this first reaction considered as an isolated step, may approximate 100%. The final physiologically necessary change of hydrogen peroxide to oxygen and water would account for the subsequent loss of efficiency in the overall process.

Thus we see that in biochemical reactions there is a continuous range of reversibility between practically 100 and 0 per cents. In no case is perpetual motion of the second kind indicated.

Discussion

It has been shown that the numerous existing published efficiency data on certain autotrophic and other coupled processes often fail both (1) to test the applicability of the second law of thermodynamics to such processes, except in the crudest manner, and (2) to measure the reversibility of each of the processes *per se* apart from accompanying but extraneous, unrelated, normal metabolic processes of the microorganisms. It might be argued, in connection with the latter objection, that since these extraneous processes have always accompanied the coupled reactions, calculations correcting the machine efficiencies (i.e., the second law efficiencies as defined by the writer) are without point. However, this circumstance may not be true in the future. Indeed, attempts are being made to isolate important coupled reactions, so that if success should attend these efforts, then the extracellular efficiency will be the second law efficiency, and the machine efficiency will then, in turn, be without point. The problem is very real, and the determination of the second law rather than the machine efficiencies very necessary, therefore, regarding what would be the efficiency of a coupled process if it were isolated from the cells and carried on independently, and accordingly the title of this paper has been made to read "coupled reactions in biological systems" rather than "coupled biological reactions." In the case of nitrogen fixation, for example, the machine efficiency is only about one per cent, whereas the second law efficiency is fifty to one hundred times this value (18), and there is good reason to believe that the process of fixation *per se* might be isolated and carried on independently of the organisms. No implication is intended, of course, that isolated coupled reactions will necessarily give exactly the same second law efficiency as when unisolated.

Summary

1. It has been the task of this paper to indicate the extent to which the applicability of the second law of thermodynamics to life processes has so far received direct *experimental* support. It is pointed out that, in general, critical data do not obtain.

2. The applicability of the law to autotrophic reduction of carbon dioxide by hydrogen has been shown to obtain very accurately to within an order of about one per cent, in the case of *Bacillus pycnoticus* Ruhland.

3. The reversibility of autotrophic reduction of carbon dioxide by hydrogen is practically perfect, 100 ± 1.2%, when the extraneous energy consumed in the metabolic processes of the organisms is corrected for.

4. The reversibilities of the more important known coupled biological reactions have been described and summarized. Few, if any, attain 100% as in the carbon dioxide-hydrogen case.

5. It is shown that with respect to the possible thermodynamic free energy efficiencies of coupled reactions occurring in biological systems two fundamentally different types obtain: those in which the work done in any given reaction is compared to the total free energy dissipated by that reaction, and those in which the work done in any given reaction is compared to the total free energy dissipated by the organisms in carrying out all their life processes. The former has been termed the second law free energy efficiency and the latter the machine free energy efficiency.

6. The hydrogen bacteria constitute one of the few cases, if not the only case, where, with respect to the entire life processes of an organism, it has been possible experimentally to account for all the free energy consumed, with an order of one per cent, i.e., where it has been possible to draw a complete free energy balance sheet between the total free energy shown to have been utilized or dissipated by the organism and that known to have been consumed by the organism.

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Washington, D. C.,
June 28, 1930.

References

[1] Thomson: Proc. Roy. Soc. Edin., March 17 (1851).

[2] Grove: "The Correlation and Conservation of Forces," by E. L. Youmans: 82 (1865).

[3] Wand: Karl's Repertorium der Exp. Physik, **4**, 390-400 (1868).

[4] Helmholtz: Sitzungsber. Akad. Wiss. Berlin, **1882**, 34.

[5] Parker: Proc. Phil. Soc. Camb., **1892**, Oct., 6.

[6] Parker: "Thermodynamics", 123 (1894).

[7] A. V. Hill: J. Physiol., **46**, 469 (1913); Nature, **113**, 859, 1924.

[8] Lewis and Randall: "Thermodynamics", Chap. 10 and 11 (1923).

[9] Guye: "Physico-Chemical Evolution" (1925).

[10] Lewis: "The Anatomy of Science", Chap. 6.

[11] Baas-Becking and Parks: Physiol. Rev., **7**, 85 (1927).

[11a] Buchanan and Fulmer: "The Physiology and Biochemistry of Bacteria", **3**, 185, lines 1-4 (1930).

[12] Donnan: J. Gen. Physiol., **8**, 688 (1927).

[13] Burk: Proc. Roy. Soc., **104** B, 153 (1929).

[13a] Watson: Science **72**, 220 (1930).

[14] Thomson: Trans. Roy. Soc. Edin., **16**, 541 (1849).

[15] Helmholtz: "Ueber die Wechselwirkung der Naturkrafte", 25 (1854).

[16] Tait: "Sketch of Thermodynamics", 56-59 (1877).

[16a] Clausius: Pogg. Ann., **120**, 426 (1863).

[17] Ruhland: Jahrbuch. wiss. Bot., **63**, 321 (1924).

[17a] Sohngen: Centr. Bakt., (2) **15**, 513 (1906).

[18] Burk and Lineweaver: To be published.

[19] Warburg and Negelein: Bio. Z., **110**, 66 (1920).

[20] Meyerhof: "Chemical Dynamics of Life Phenomena" (1924).

[21] Clifton and Ort: J. Phys. Chem., **34**, 855 (1930).

[22] Angerer: Arch. Hyg., **88**, 139 (1919).

[23] Ludwig: Arch. Protistenkunde, **62**, 13 (1928).

[24] H. T. Brown: Ann. Bot., **28**, 197 (1914).

[25] Hartree and Hill: Proc. Roy. Soc., **103** B, 243, 249 (1928).

[26] Hartree and Hill: Proc. Roy. Soc., **104** B, 1 (1928).

STUDIES ON ELECTROKINETIC POTENTIALS. VII

The Temperature Coefficient of the ζ-Potential*

BY HENRY B. BULL AND ROSS AIKEN GORTNER

Historical

Burton[1] determined the velocity of migration of silver particles in water at 11.0° and 21.0° C. He found that the velocities of the particles were 19.6×10^{-5} cm./sec. and 25.2×10^{-5} cm./sec., respectively, at these two temperatures, indicating a decided temperature coefficient, However, when these values were multiplied by the corresponding viscosities for these temperatures, he obtained 0.251 and 0.250 respectively.

Cruse[2] studied the electro-osmosis of distilled water through diaphragms of clay between 10° and 60°. He found a marked maximum for the rate of flow of water at about 38.0°. He did not correct for the change of conductivity, the viscosity, or the dielectric constant with the temperature, which as has been pointed out by Smoluchowski[3] must be taken into consideration.

Gee and Harrison[4] found with the streaming potential a decided maximum for H/P around 40° for wool, cotton, and silk against distilled water. Their experiments cover a range from 16° to 84°. They made no efforts to correct for the change of the conductance, the dielectric constant, or the viscosity, but they do point out that the factor $\eta\kappa/D$, where η is the viscosity, κ the specific conductance of water, and D the dielectric constant is approximately a constant from 15° to 70°. These results would indicate that the observed changes in H/P are accompanied by a corresponding change in the ζ-potential. It may be pointed out, in criticism of Gee and Harrison's work, that for the specific conductivity they used the specific conductance of distilled water and took no account of the surface conductance which may entirely invalidate their conclusions.

Briggs, Bennett, and Pierson[5] found no suggestion of a maximum for the rate of flow of water through a diaphragm of cellulose with electrical osmosis between 22° and 67°, but found rather a steady increase with the temperature. When the rate of water flow was multiplied by the corresponding viscosities at the different temperatures, a steady decrease was obtained. No account was taken of the change in conductivity.

Experimental

The apparatus and technic used were identical with those of our previous paper[6] and involved only slight modifications from those used by Martin and Gortner[7], which in turn were a modification of Briggs'[8] methods

In order to measure the temperature coefficient of the streaming potential, a constant temperature air bath was installed. It was 150 cm. in length, 60 cm. wide, and 60 cm. deep. The air was circulated over a series of heating coils by means of an electric driven Sirocco fan. It was possible to regulate the temperature to ±0.1° The streaming potential cell was placed inside the air bath and shielded wires brought out to the electric measuring apparatus. Before making a determination, the bath was brought to the desired temperature with the cell in place and allowed to remain at this temperature for one hour before a measurement was attempted.

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Some difficulty was expected from the change of the cell constant of the diaphragm with temperature. It was thought that the cellulose might become more hydrated with increasing temperature, with a result that the fibers would swell and change the cell constant of the diaphragm. This was found not to be the case, as is adequately demonstrated by the data in Table I.

The ethyl alcohol used was freshly distilled over metallic sodium. The alcohol was found to be extremely hygroscopic, and considerable care was exercised in order to protect it from the moisture of the air. Both the inlet and the outlet of the streaming cell were connected to absorption towers of barium perchlorate, so the alcohol in the cell was at all times protected from the moisture of the air. The cellulose was allowed to remain for two weeks in contact with absolute ethyl alcohol before the determination was attempted

The Cell Constants of the Cellulose Diaphragm in Relation to Temperature

TABLE I

Temperature o°C	Cell Constant of Diaphragm	Temperature o°C	Cell Constant of Diaphragm
Diaphragm No. 1		Diaphragm No. 2	
24.8	1.318	24.8	0.891
25.0	1.311	25.0	0.905
30.4	1.296	31.5	0.913
31.5	1.321	37.2	0.904
37.2	1.288	44.0	0.900
44.0	1.320	50.4	0.897
50.4	1.288		

The resistance of the diaphragm could not be measured with any degree of precision with the usual conductivity apparatus because the resistance was too high. A Leeds and Northrup alternating-current galvanometer was accordingly employed in place of the usual head phones. An accuracy with less than 1% error was possible.

The data for the change of the specific conductance, the ratio of the observed electromotive force to the pressure, the factor $H\kappa_s/P$, the viscosity, the dielectric constant and the ζ-potential are given for ethyl alcohol-cellulose, distilled water-cellulose and an aqueous solution of $0.1 = 10^{-3}$ N NaCl with various temperatures. Certain of these results are graphed. The values of the coefficient of viscosity were obtained from the International Critical Tables. The dielectric constant for water at the various temperatures was calculated from Drude's[9] formula. The dielectric constant for 0.1×10^{-3} N NaCl was assumed to be equal to that of water. The dielectric constant and its change with temperature for ethyl alcohol was obtained from the International Critical Tables.

The data for ethyl alcohol-cellulose interface are shown in Table II and summarized in Table III and Figs. 1, 2, 3, and 4.

The data for the water-cellulose interface are given in Table IV and summarized in Table V and Figs. 5, 6, 7, and 8.

The data for the 0.1×10^{-3} N NaCl solution against cellulose are shown in Table VI and summarized in Table VII and Figs. 9, 10, 11, and 12.

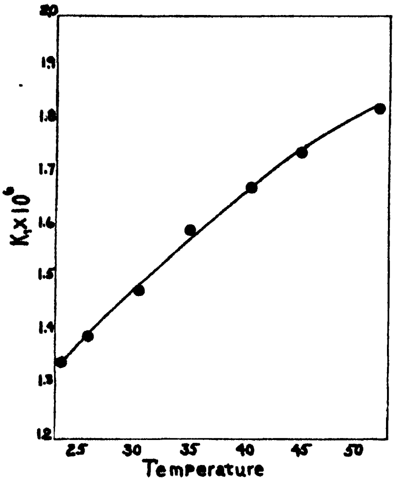

FIG. 1

Showing the relation between the specific conductivity of ethyl alcohol in the diaphragm and the temperature.

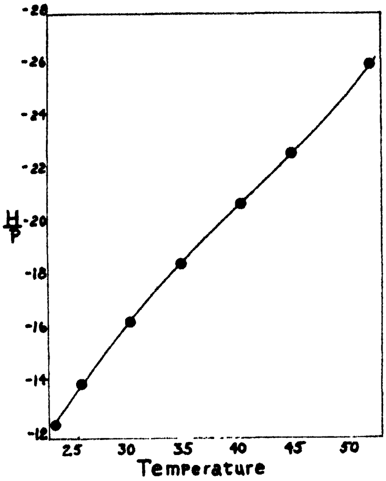

FIG. 2

Showing the relation between $\frac{H}{P}$ and the temperature for an ethyl alcohol-cellulose interface.

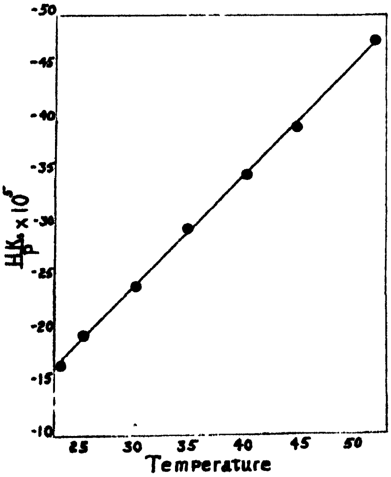

FIG. 3

Showing the relation between $\frac{H_{Ks}}{P}$ and the temperature for an ethyl alcohol-cellulose interface.

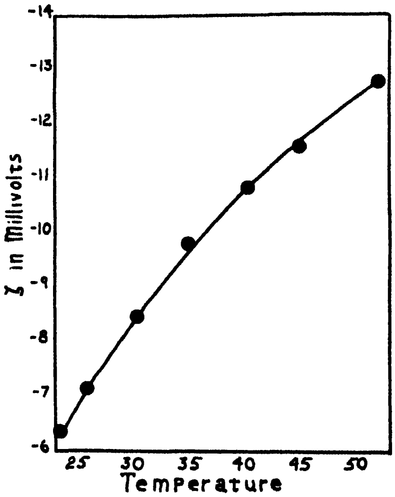

FIG. 4

Showing the relation between ζ-potential of an ethyl alcohol-cellulose interface and temperature.

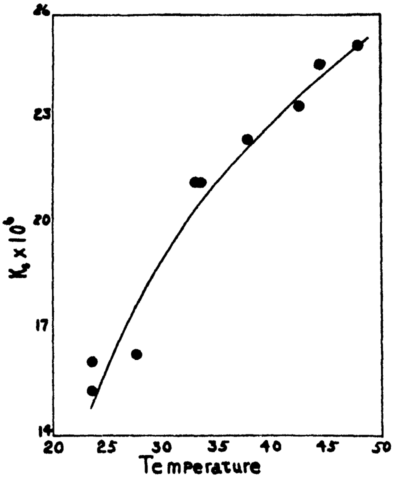

FIG. 5
Showing the relation between the specific conductivity of water in the diaphragm and the temperature.

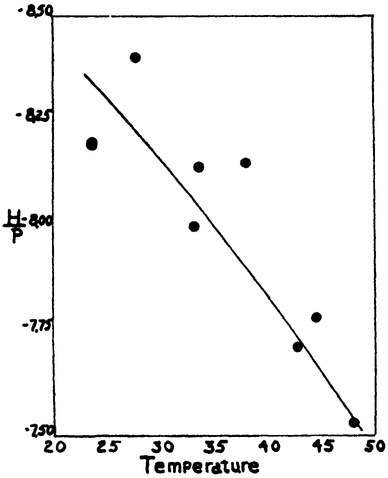

FIG. 6
Showing the relation between $\frac{H}{P}$ and the temperature for a water-cellulose interface.

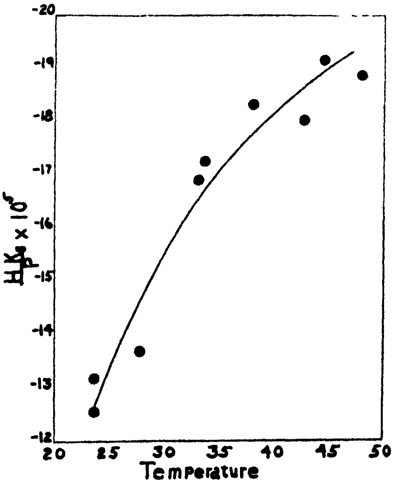

FIG. 7
Showing the relation between $\frac{H_{KS}}{P}$ and the temperature for a water-cellulose interface.

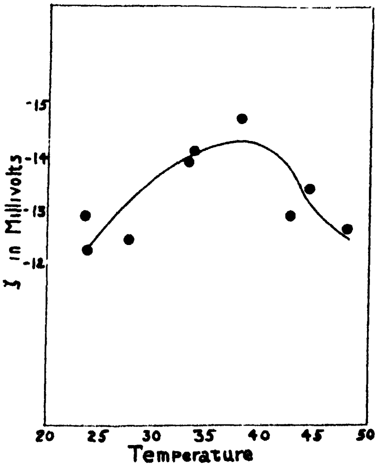

FIG. 8
Showing the relation between the ζ-potential and the temperature at a water-cellulose interface.

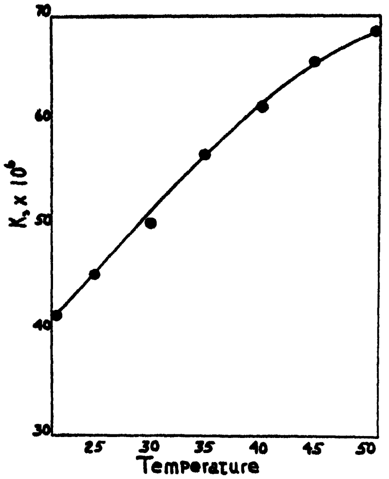

FIG. 9

Showing the relation between the specific conductivity of 0.1 × 10^{-3} N solution of NaCl in the diaphragm and the temperature.

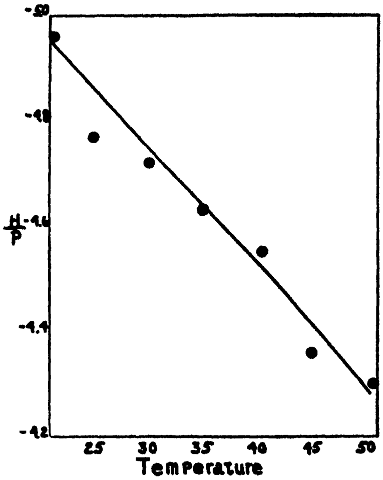

FIG. 10

Showing the relation between $\frac{H}{P}$ and the temperature for a 0.1 × 10^{-3} N NaCl-cellulose interface.

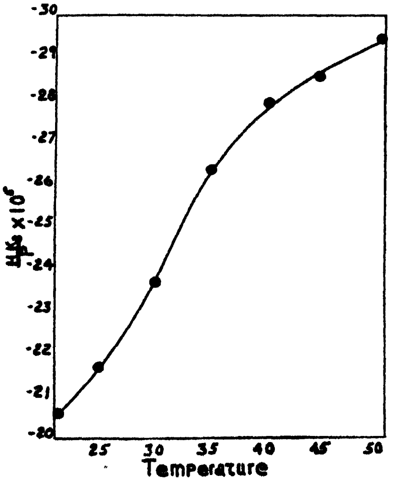

FIG. 11

Showing the relation between $\frac{H_{KS}}{P}$ and the temperature for a 0.1 × 10^{-3} N NaCl-cellulose interface.

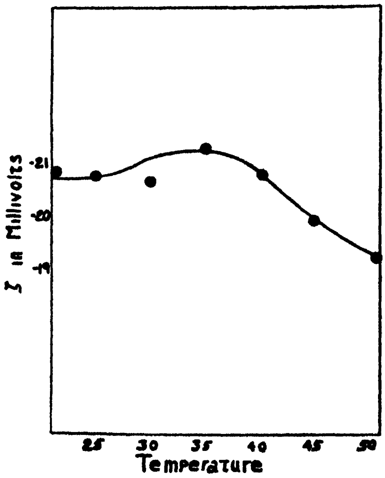

FIG. 12

Showing the relation between the ζ-potential and the temperature at a 0.1 × 10^{-3} N NaCl-cellulose interface.

Discussion

It is clear from the results that we have a marked positive temperature coefficient for the ζ-potential at an ethyl alcohol-cellulose interface. The cause of this change of ζ with temperature is not known.

Table II

Data for Ethyl Alcohol-Cellulose Interface

Temperature O°C.	Pressure cm.Hg	H/P	Pressure cm. Hg	H/P
23.5	29.7	−12.51	29.7	−12.63
	33.7	−12.53	33.6	−12.42
	37.9	−12.36	37.7	−12.45
		Average H/P = −12.483		
26.0	34.4	−14.04	20.5	−13.58
	37.9	−13.97	25.1	−13.78
	41.1	−14.03	30.7	−13.77
		Average H/P = −14.011		
30.4	28.0	−16.66	31.5	−16.47
	32.4	−16.38	35.9	−16.42
	34.9	−15.84	39.1	−16.54
		Average H/P = −16.385		
35.0	18.2	−18.43	27.5	−19.07
	23.7	−18.65	30.6	−18.59
	29.4	−18.62	37.7	−18.09
		Average H/P = −18.58		
40.5	23.7	−21.29	23.0	−20.52
	29.9	−21.17	28.5	−20.75
	33.8	−20.53	35.3	−20.62
		Average H/P = −20.81		
44.9	20.9	−23.09	21.3	−23.10
	26.9	−22.81	27.1	−22.54
	33.8	−22.25	32.0	−21.97
		Average H/P = −22.62		
52.1	29.8	−25.72	24.9	−26.67
	21.5	−26.39	30.0	−26.06
	26.5	−26.13	33.0	−25.47
		Average H/P = −26.07		

TABLE III

Summary of Data for Ethyl Alcohol

Temperature o°C.	$\kappa_s \times 10^6$ mhos	H/P	$\frac{H\kappa_s}{P} \times 10^5$	η poise	D	ζ mv.
23.5	1.345	−12.483	−16.78	0.01125	25.12	−6.370
26.0	1.393	−14.011	−19.51	0.01073	24.72	−7.178
30.4	1.480	−16.385	−24.24	0.00995	24.05	−8.501
35.0	1.596	−18.58	−29.65	0.00915	23.40	−9.8275
40.5	1.673	−20.81	−34.82	0.00830	22.65	−10.816
44.9	1.738	−22.62	−39.32	0.00768	22.06	−11.603
52.1	1.826	−26.07	−47.50	0.00670	21.10	−12.785

TABLE IV

Data for Water-Cellulose Interface

Temperature °C.	Pressure cm. Hg	H/P	Temperature °C.	Pressure cm. Hg	H/P
23.7	69.5	−8.316	27.6	74.4	−8.474
	73.1	−8.194		79.7	−8.393
	81.9	−8.113		84.1	−8.359
Average H/P =		−8.207	Average H/P =		−8.408
33.6	76.1	−8.258	38.0	70.8	−8.114
	80.5	−8.136		77.1	−8.035
	85.5	−8.023		82.6	−8.293
Average H/P =		−8.139	Average H/P =		−8.147
42.6	77.7	−7.786	48.0	70.9	−7.637
	81.9	−7.710		79.2	−7.525
	85.1	−7.655		84.6	−7.432
Average H/P =		−7.717	Average H/P =		−7.534

TABLE V

Summary of Data for Water-Cellulose Interface

Temperature °C.	$\kappa_s \times 10^6$ mhos	H/P	$\frac{H\kappa_s}{P} \times 10^5$	η poise	D	ζ mv.
*23.6	16.09	−8.199	−13.19	0.00924	79.30	−13.02
23.7	15.30	−8.207	−12.55	0.0092	79.30	−12.34
27.6	16.29	−8.408	−13.69	0.00843	77.90	−12.55
*33.1	21.149	−7.993	−16.90	0.00746	75.98	−14.06
33.6	21.20	−8.139	−17.25	0.0074	75.85	−14.26
38.0	22.44	−8.147	−18.28	0.00679	74.36	−14.12
42.6	23.35	−7.717	−18.02	0.00622	72.88	−13.03
*44.5	24.61	−7.785	−19.15	0.00602	72.25	−13.52
48.0	25.07	−7.534	−18.88	0.00567	71.20	−12.75

* These determinations were made several months after the other data recorded in the table.

TABLE VI

Data for 0.1 × 10^{-3} N NaCl

Temperature °C.	Pressure cm. Hg	H/P	Pressure cm. Hg	H/P
21.35	71.2	−4.985	81.3	−4.913
	77.7	−5.019	85.4	−4.894
	82.9	−5.012	73.0	−4.952
			Average H/P = −4.962	
25.05	78.0	−4.839	77.7	−4.738
	82.0	−4.823	82.5	−4.715
	85.8	−4.841	85.7	−4.708
			Average H/P = −4.777	
30.15	78.2	−4.642	66.3	−4.849
	82.4	−4.624	76.1	−4.803
	85.7	−4.626	81.7	−4.779
			Average H/P = −4.720	
35.15	81.7	−4.645	79.4	−4.622
	84.5	−4.633	82.9	−4.620
	74.1	−4.662	85.4	−4.637
			Average H/P = −4.636	
40.3	80.1	−4.544	81.6	−4.589
	82.5	−4.527	83.8	−4.600
	85.5	−4.519	86.5	−4.595
			Average H/P = −4.561	
45.0	79.2	−4.362		
	82.1	−4.354		
	85.7	−4.378		
	Average H/P = −4.364			
50.6	80.8	−4.288		
	83.7	−4.289		
	85.9	−4.324		
	Average H/P = −4.300			

TABLE VII

Summary of Data for 0.1 × 10^{-3} N NaCl

Temperature °C.	$\kappa_s \times 10^6$ mhos	H/P	$\frac{H\kappa_s}{P} \times 10^5$	η poise	D	ζ mv.
21.35	41.4	−4.96	−20.57	0.00976	81.25	−20.94
25.0	45.4	−4.77	−21.70	0 00894	78.8	−20.87
30.1	50.27	−4.72	−23.73	0 00793	76.95	−20.73
35.1	56.89	−4.63	−26.37	0.00718	75.26	−21.35
40.4	61.20	−4.56	−27.91	0.00649	73.62	−20.86
45.0	65.54	−4.36	−28.60	0.00597	72.12	−20.07
50.6	68.55	−4.30	−29 47	0.00544	70.42	−19.30

If we treat the Helmholtz double layer as a condenser, we have the relation

$$\zeta = \frac{4 \pi q d}{D}$$

where:

q is the charge per unit area on the plates of the condenser,

d is the thickness of the double layer, *i.e.*, the distance between the plates of the condenser,

D is the dielectric constant.

Substituting the values for ζ and D at the various temperatures, we have the values for $4 \pi q d$ shown in Table VIII.

These results show that as we increase the temperature, we increase either the charge or the thickness of the Helmholtz double layer, or perhaps both the charge and the thickness increase with increasing temperature.

The temperature coefficient of the ethyl alcohol-cellulose system is of sufficient magnitude to require consideration in precise work.

As is shown in Figs. 8 and 12 the ζ-potential for both pure water-cellulose and 0.1 × 10^{-3} N NaCl cellulose interface exhibit a maximum around 38°C.

Again employing the relation

$$\zeta = \frac{4 \pi q d}{D}$$

we have, upon substituting the known values for ζ and D at the various temperatures, results for $4 \pi q d$ shown in Table IX.

Both water-cellulose and 0.1 × 10^{-3} N NaCl interfaces show a slight maximum for the function $4 \pi q d$ around 40°, although the values show less variation with temperature than does the ζ-potential.

It is clear from these results that the temperature coefficient of the ζ-potential is much different from that for the electrode potential or Freundlich's so-called thermodynamic potential, which is an additional argument in favor of the view of their independence of each other.

Table VIII

The Effect of Temperature on the Electrical Forces acting at a Cellulose-Ethyl Alcohol Interface

Temperature °C.	$4 \pi q d$	Temperature °C.	$4 \pi q d$
23.5	160.0	40.5	244.9
26.0	177.4	44.9	255.9
30.4	204.4	52.1	269.7
35.0	229.9		

Table IX

The Effect of Temperatures on the Electrical Forces acting at Cellulose-Water and Cellulose-Salt Solution Interfaces

Pure Water		0.1×10^{-3} N NaCl	
Temperature °C.	$4 \pi q d$	Temperature °C.	$4 \pi q d$
23.7	97.8	21.3	170.1
27.6	97.7	25.0	164.4
33.6	108.1	30.1	159.5
38.0	110.4	35.1	160.6
42.6	94.9	40.4	153.5
48.0	90.7	45.0	144.7
		50.6	135.9

It is suggestive that the maximum for the ζ-potential for the pure water and for the 0.1×10^{-3} N NaCl comes at about 40° which is also the point for the minimum specific heat of water.

Summary

1. The temperature coefficients of the ζ-potential for the interfaces, water-cellulose, 0.1×10^{-3} N NaCl-cellulose, and ethyl alcohol-cellulose, have been investigated between 20° and 51°.

2. A marked positive temperature coefficient is exhibited by the ζ-potential at an ethyl alcohol-cellulose interface. The relationship, however, is not strictly linear, the temperature coefficient varying from approximately 0.31 mv. per degree in the range from 23.5° to 30.4° to 0.16 mv. in the range 44.9° to 52.1°.

3. The aqueous systems investigated show a much lower temperature coefficient than the ethyl alcohol-cellulose system. A maximum at about 40° was found for the temperature coefficient for the ζ-potential at both a water-cellulose and a 0.1×10^{-3} N NaCl-cellulose interface. For all practical purposes the temperature coefficient of aqueous systems can be ignored in streaming potential measurements made under ordinary laboratory conditions, since in small temperature ranges the temperature effect is much smaller than is the experimental error of the determination.

Literature Cited

[1] E. F. Burton: On the Properties of Electrically Prepared Colloidal Solutions, Phil. Mag., (6) **11**, 425-447 (1906.)

[2] A. Cruse: Über die elektrische Kataphorese des destillierten Wasser durch poröse Tondiaphragmen (Pukallmasse), insbesondere ihre Abhangigkeit von Temperatur und Stromdichte, Physik. Z., **6**, 201-204 (1905).

[3] M. von Smoluchowski: Zur Theorie der elektrischen Kataphorese und der Oberflächenleitung, Physik. Z., **6**, 529-530 (1905).

[4] W. W. H. Gee and Wm. Harrison: The Electrical Theory of Dyeing, Trans. Faraday Soc., **6**, 42-70 (1910).

[5] T. R. Briggs, H. S. Bennett and H. L. Pierson: Electrical Endosmose II, J. Phys. Chem., **22**, 256-272 (1918).

[6] H. B. Bull and R. A. Gortner: Studies on Electrokinetic Potentials. VI. Electrical Phenomena at Interfaces, Eighth Colloid Symposium Annual, J. Phys. Chem., **35**, 307 (1931).

[7] W. McK. Martin and R. A. Gortner: Studies on Electrokinetic Potentials. V. Interfacial Energy and the Molecular Structure of Organic Compounds. 1. Electrokinetic Potentials at Cellulose-Organic Liquid Interfaces, J. Phys. Chem., **34**, 1509-1539 (1930).

[8] D. R. Briggs: The Determination of the ζ-Potential on Cellulose—A Method, J. Phys. Chem., **32**, 641-675 (1928).

[9] P. Drude: Der elektrische Brechungsexponent von Wasser und wässerigen Lösungen, Ann. Physik Chem., **59**, 17-62 (1896).

WALL STRUCTURE AND MINERALIZATION IN CORALLINE ALGAE*

L. G. M. BAAS-BECKING AND E. WAYNE GALLIHER

1. Introduction

In the last few decades an intensive study has been made of plant and animal membranes; particularly of their optical properties. This study was really, in a way, a revival of the older polariscopic methods of von Ebner,[5] Valentin,[24] and Naegeli,[18] reinforced by the modern X-ray methods.

It seems that, especially in the German school, the evidence obtained is applied to explain the phenomena in the light of Naegeli's micellar theory, according to which the building blocks of the membranes should be elongated, anisotropic and "crystalline" bodies.

The results of polariscopic work of Ambronn,[1] and also of Frey,[6,7] and their school are invariably explained by the existence of micellae and Frey goes so far as to say, in his paper on the structure of plant membranes, "die Theorie von Naegeli, die als Bausteine der Membranen längliche, optisch-anisotrope kristalline Mizelle forderte, darf daher in allen ihren Teilen als bewiesen gelten."

Now neither the polariscopic investigations of Heringa and Minnaert[10] on the animal tendon nor the X-ray evidence obtained by Sponsler[23] on plant fibers seems to suggest the presence of supra-molecular discrete and discontinuous units. It seemed desirable to apply the methods of the German school to other membranes because, in the first place, their work represents a decidedly new departure, inspiring, stimulating, and apparently almost unknown in this country (see, however, McNally and Sheppard).[14] In the second place, it seemed worth while to see in how far the presence of micellae is suggested by the experimental data and to what extent the phenomena could be explained without them.

For investigation of this question the coralline algae offered an interesting possibility because their cell walls are non-cellulosic (Oltmanns,[19] III, p. 2) and, under certain conditions, incrustated with carbonates of calcium and magnesium. The polariscopic study of these cell walls in their mineralized as well as in their decalcified state might lead not only to suggestions about the structure of the organic wall but also to the way in which the carbonate crystals are deposited.

Furthermore, especially in the mineralized material, the X-ray analyses would give an ultimate test as to the reliability of the polariscopic findings.

2. The Material and Its Properties

In our work we have used almost exclusively *Corallina officinalis Lamarck* and *Amphiroa dorbigniana Decaisne*. Preliminary work showed that the mineralized membranes of *Melobesia*, *Lithothamnion*, *Lithophyllum* and

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*Jacques Loeb Laboratory of Stanford University, California.

Lithothrix have similar optical characteristics. *Corallina* and *Amphiroa* are both very common near the marine station. They have the additional advantage that they possess unmineralized internodes or genicula. The nodes or articula consist of thick-walled cells, particularly suited for polariscopic work. These cells originate either from embryonic cells in which rapid dehydration causes formation of a heavy wall or from calcified cells from which the minerals are removed secondarily. The mature geniculum represents a group of dead cells (analogy with mechanical tissues in higher plants) which gives flexibility to the alga which would otherwise be unable to withstand the continuous beating of the surf.

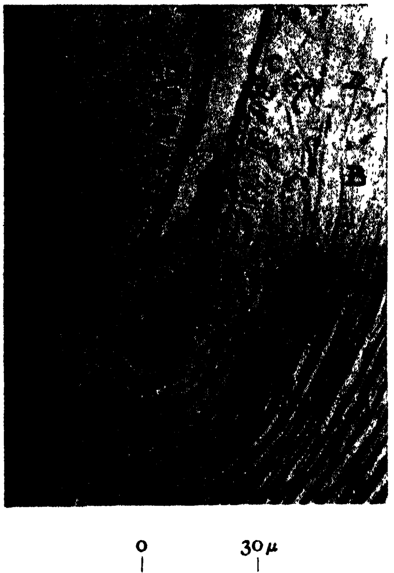

FIG. 1
Corallina officinalis L., decalcified longitudinal section, stained with ruthenium oxychloride. Leitz 3 mm. oil, ocular 20×. A, genicular fibres; B, articular fibers; C, cortical tissue.

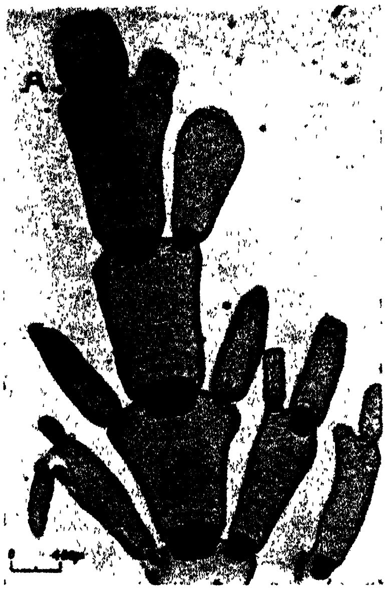

FIG. 2
Corallina officinalis L., decalcified longitudinal stained with ruthenium oxychloride. The young genicula (at A) are still thin-walled. Obj. 6, Zeiss; ocular 10×.

In Fig. 1, A marks the genicular tissue, B the particular central fibers, while the plastids are plainly visible in the cortex C. The pitting of the central fibers is indicated at D.

We are indebted to Lois Wilbur Hopper for the preparation of the microtome sections used in this research.

3. Chemical Nature of the Wall Substance

Oltmanns[19] (III, p. 2) states that a great variety of substances seem to collaborate in the formation of the algal cell-walls. It is, however, difficult to translate names like "callose," "pectin" into definite chemical pictures. The cell walls of the Corallines have the following properties:

They are:	Interpretation:
1) Insoluble in ammoniacal copper	1) Non-cellulosic
2) Soluble in alkali	2) Non-cellulosic
3) Stain with ruthenium-oxychloride	3) "Mangin reaction" on pectins
4) Stain with anilin blue	4) Callose; pectin?
5) Yield CH_3I on distillation with HI	5) Methoxy group present; pectin?
6) Opaque to ultra violet light	6) Non-cellulosic

From this it follows that the walls are non-cellulosic and contain appreciable amounts of pectin-like substances.

Fig. 2 shows a longitudinal, decalcified section of *Corallina* which has been stained with ruthenium oxychloride. The genicular walls seem to stain better than the articular walls. This is primarily due to their greater thickness. At A, where the walls in the young geniculum are still thin, the intensity of the stain is approximately equal to that of the articular fibers.

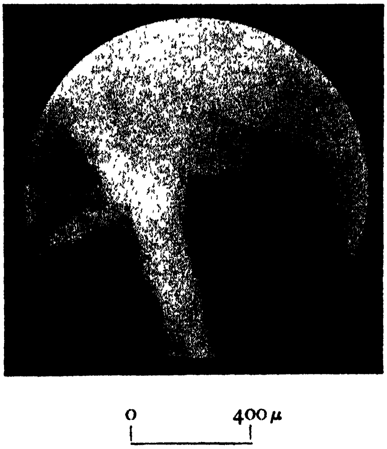

FIG. 3
Amphiroa dorbigniana Decaisne, decalcified longitudinal section, unstained. Photographed in ultra-violet light. Filter Corning "violet ultra"; obj. Zeiss quartz, 2.5 mm.; glycerol immersion; ocular Zeiss quartz 5×.

Frey, in his paper on the structure of cell-walls in higher plants has made use of the fact that cellulose is transparent to ultraviolet light. A photograph of a plant section, therefore, will show the non-cellulosic material as dark structures, the cellulose remaining transparent. Photograms of the genicula of *Amphiroa* confirmed our opinion that the material is non-cellulosic (see Fig. 3). In our experiments we used Zeiss quartz optics, obj. 2.5 mm., ocular × 5 natural quartz throughout, quartz slide and cover slip and glycerol immersion. As a source of light we used the Hashimoto[9] quartz mercury lamp which is a simple and inexpensive source of ultraviolet light and which showed itself to be particularly adapted to microphotography. We are indebted to Mr. T. Hashimoto, research chemist of the Hopkins Marine Station, Jacques Loeb Laboratory, for collaboration in these experiments. The light was filtered through a Corning "Violet Ultra" screen 9.45 mm. filter. Even in reflected light, about 20 centimeters removed, we found that a 5-10 second exposure was fully sufficient.

4. Optical Properties of the Membrane

The genicular fibers as well as the decalcified articular fibers show a strong positive birefringence under crossed nicols in longitudinal sections (see Fig. 4). The walls of the fibers seem totally dark in cross section (see Fig. 6). As this phenomenon had nothing whatsoever to do with mineral deposition we were led to consider its various possible causes. Pectin, according to Molisch[17] and Frey[7] is isotropic. Are the phenomena observed in the Corallines compatible with this view, or should we conclude that the fiber does not consist of pectin?

The refractive index of the fiber proved, according to Becke's method, to be 1.534 ± .002. If the properties of the hypothetical crystallites were different, it did not appear from these tests. The index is higher than that of chitin, lower than that of cellulose, and about equal to that of fibrous aluminum hydroxide.

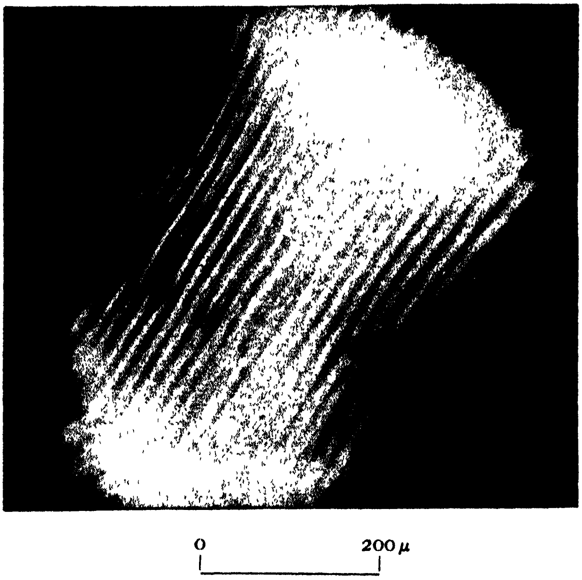

FIG. 4
Geniculum of *Corallina* observed in diagonal position under crossed nicols. Obj 3 mm. oil; ocular 20×.

There are a great many causes for anisotropy apart from crystallinity. It would fall outside of the scope of this paper to discuss all of them. It may be said, however, that not only factors or forces influencing "directedness," such as tensions and currents, but also the form itself of the constitutional units in the material might contribute to the causation of optical anisotropy. This factor of "Formdoppelbrechung" was clearly recognized by the older authors, but it is only since theoretical work of Wiener,[25] and its application by Moehring[16] for chitin, Frey[7] for cellulose and other plant membranes, and a multitude of other authors, that we are able to interpret birefringence due to position of submicroscopic elements.

For a full discussion of these matters we refer to the original papers. It will suffice here to state the principle upon which the analysis is based. If, in a material system, ("Mischkörper" of Wiener) a mixed body, the disperse phase consists of parallel circular cylinders, the diameter of which is small in relation to the wave length of light, and if these cylinders have a refractive index of n_1 and the continuous phase (imbedding medium) n_2, the system will be birefringent and will behave as an optically uniaxial body. The strength of the birefringence is a function of n_2^2 and n_1^2 and, of course, of the wave length of the light used and the thickness of the preparation. Should the disperse phase be arranged as parallel vertical lamellae (comp. Fig. 7) instead of parallel cylinders the same consideration holds except that the optical character is reversed.

In both cases we may plot $\Gamma\lambda/d$ (in which Γ is retardation in $m\mu$, λ wave-length in $m\mu$), against the n_2 of the imbedding medium. If the curve approaches zero for a certain value of n_2 we might say that in this case $n_2 = n_1$ and the disperse elements were optically isotropic. If, however, the curve either finds its minimum below or above the abscissa, we have evidence of true micellary birefringence, in the former case optically negative, in the latter of a positive nature.

It should be noted that, in Wiener's theory, the refractive index as such is not mentioned, but the dielectric constant which is assumed to be equal to the square of the refractive index, is used. In Wiener's general equation there appear the following components:

ϵ_m, the dielectric constant of the mixed body;

ϵ_1 and ϵ_2 respectively the dielectric constants of the first and second component element;

δ_1 and δ_2 respectively the fractional volume of the first and second component element; and

μ, which is called the form-coefficient and which is definite and different for any configuration.

For spheres in a continuum we have $\mu = 2\epsilon_2$, but for anisodiametric particles (cylinders or rods), parallel to the optical axis $\mu = \infty$, perpendicular to the optical axis $\mu = \epsilon_2$; for lamellae these values are $\mu = 0$ parallel and $\mu = \infty$ perpendicular to the optical axis.

By means of these values for μ, substituted in the general equation

$$\frac{\epsilon_m - \epsilon_2}{\epsilon_m + \mu} = \delta_1 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \mu}$$

we can get $\epsilon_m = \epsilon_p$ in one, and $\epsilon_m = \epsilon_s$ in another direction. In this fashion we get, for the configuration-birefringence of rods

$$\epsilon_p - \epsilon_s = + \frac{\delta_1 \delta_2 (\epsilon_1 - \epsilon_2)^2]}{(\delta_1 + 1)\epsilon_2 + \delta_2 \epsilon_1}$$

and for the configuration-birefringence of lamellae

$$\epsilon_p - \epsilon_s = - \frac{\delta_1 \delta_2 (\epsilon_1 - \epsilon_2)^2}{\delta_1 \epsilon_2 + \delta_2 \epsilon_1}$$

The sign means that rods in general cause positive birefringence, lamellae negative birefringence. However, if rods are arranged in a fascicular fashion instead of in layers, the sign of the birefringence is inverted. It is better, therefore, to speak about "linear" and "stratified" configuration-birefringence than to talk about "bacillary" and "lamellary" birefringence.

As there is no way to determine $n_a - n_o$ from $n_a^2 - n_o^2$, both factors being variable, we might consider

$$\begin{aligned} (n_a - n_o)^2 &< n_a^2 - n_o^2 < (n_a + n_o)^2 \text{ or} \\ n_a - n_o &< \sqrt{n_a^2 - n_o^2} < n_a + n_o \\ n_a - n_o &< \sqrt{(n_a - n_o)(n_a + n_o)} < n_a + n_o \end{aligned}$$

or the harmonic mean between $n_a - n_o$ and $n_a + n_o$.

From our experimental data we may derive $n_a - n_o$ and dividing $n_a^2 - n_o^2$ (calculated from the equation) by this amount we should get $n_a + n_o$ and accordingly n_a and n_o may be determined. The values derived in this way are exceedingly improbable, showing that the theory of Wiener cannot be applied quantitatively to our data.

In Wiener's equation for bacillary birefringence $\epsilon_p - \epsilon_s > 0$. In this case Wiener claims that the birefringence $n_a - n_o$ is always positive. It goes without saying that if $n_a > n_o$, $n_a^2 > n_o^2$; but it is not quite clear how n_a^2 may be regarded as a measure of ϵ_p. For it has been repeatedly shown (cf. Pockels,[20] p. 69) that Maxwell's relation, giving the velocity of an electromagnetic disturbance in a certain substance,

$$g = \frac{c}{\sqrt{\epsilon\mu}}$$

(in which c is the velocity of light, μ the magnetic permeability, and ϵ the dielectric constant) only holds for a few cases and only in a very approximate way. The refractive index in general, if no anomalous dispersion influences the result, may be expressed by

$$A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \text{ .... which limits to A for } \lambda = \infty.$$

A^2 should equal the dielectric constant. Neglecting the higher terms, and using the relation $A + B/\lambda^2$ Pockels calculates the agreement between n_α, n_β, and n_γ for sulphur and the dielectric constants determined by Boltzmann. In this case, in which correction was made for the λ, the discrepancies between the calculated and observed values amounted to 3-6 per cent.

Wiener states specifically (p. 600) "die vorliegende Theorie bezieht sich auf ruhenden Körper von ganz bestimmter unveränderlichen Dielectrizitätsconstanten."

From the foregoing it follows that, in general, Wiener's equation is useful as long as we remember that we can not apply it quantitatively in the majority of cases. It may give us a clue however as to the configuration of certain colloids and other substances that may be impregnated with liquids of different refractive indices.

In the following experiments we have followed closely the directions of Ambronn and Frey,[2] whose beautiful book has been a constant source of inspiration to us. We have imbedded, in various media of known refractive index, longitudinal sections of the genicular fibres of *Corallina* and *Amphiroa.* The thickness of the section was ascertained and the retardation in the various media determined by means of a Berek compensator for white light, and for red, yellow, and blue light of wavelengths 656, 589, and 486 mμ ± 5 mμ respectively. The small Leitz monochromator was used to advantage in this work. Care was taken to assure complete imbedding, as incomplete penetration is the greatest source of error in this method. The following media were used:

Medium	n_D	Medium	n_D
Air	1.00	Oil cedar	1.51
Ether vapor	1.09	Oil cassia	1.60
Water	1.33	Carbon bisulphide	1.63
Oil paraffin	1.46	Monobromnaphthalene	1.65
Xylene	1.50		

While one may obtain a great many liquids with a refractive index from water (1.33) upward, there are, as yet, no media available with indices situated between air and water. However, it was found that vapors, when applied with some caution, make excellent "imbedding media" within the desired range. We have made use of ethyl ether. The procedure was as follows: a nickel chamber was prepared with two outlets and a glass bottom. A circular hole in the top allowed the mounting of a coverslip with the preparation. The coverslip was sealed onto the chamber by means of water glass. One outlet of the chamber was connected with a vacuum pump; the other with a bottle containing ethyl ether. After the ether was brought to boil and most of it evaporated the chamber was isolated and the optical retardation of the fibers in the preparation determined in the usual way.

Using the values of Lorenz from Landolt-Börnstein for ethyl ether, $n_D = 1.158$ at 0°C and 760 mm pressure, and those of Ramsay (from the same tables) for the vapor-pressure of ethyl ether at 20°C = 438 mm pressure, the refractive index of ether vapor in our experiment appeared to be

$$n_D = \frac{(n_{o \cdot 760} - 1).438}{(1 + \alpha t)\ .760} + 1 \text{ or } n_D = 1.085$$

The retardations determined in this medium in no way disturbed the continuity of our curve. We therefore believe that the procedure, while not yet entirely capable of giving absolute results, is worthy of future consideration.

The use of water may be, under certain conditions, objectionable. Whenever the fiber absorbs water, it may swell and even if the individual solid elements are not affected, the relation between the volume elements of the phases would be materially changed.

Comparatively small differences in δ_1 would give rise to large discontinuities in the curve (as may be calculated from Wiener's equation). The effect of swelling, which, moreover could not be determined microscopically, may contribute but little.

The accuracy of the method remains to be discussed. As in all subjective methods it is liable to the maximum number of errors, as the personal equation itself is a sum of disturbing factors. M. Berek[3] (p. 430) has shown that his compensator is able to record retardations of the order of magnitude of 3 mμ. The limit of birefringence actually observable with fibres of about 5000 mμ thickness would be 0.0008. Actually readings below $\Gamma\lambda/d = 0.002$ are difficult to perform. The genicular fibers, because of their greater thickness, are therefore better adapted for quantitative work on retardation, as $\Gamma\lambda$ increases linear with an increase in *d*.

It might be useful to illustrate the accuracy of the Berek method by a laboratory protocol:

$\Gamma\lambda/d$ for different fibers in air

	656mμ	589mμ	486mμ
Fiber No. 1	.0137	.0132	.0106
2	.0138	0112	.0114
3	.0130	.0125	.0110
4	.0143	0138	.0108
Average	.0137 ±0.0007	.0127 ±0.0015	.0110 ±0 0004

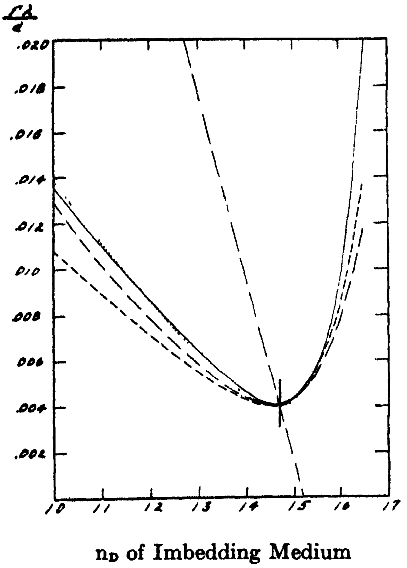

Fig. 5

Retardation of genicular fibers of *Amphiroa dorbigniana* Decaisne, plotted against the index of imbedding medium. Inclined axis dashed; heavy line indicates limit of accuracy of determinations

White Light ————
656 mμ . . . .
589 mμ — · — · —
486 mμ — — — — —

Hence the average accuracy amounted to about 0.001. Fig. 5 shows the experimental results. The curves are hyperbolic, the symmetry axis is inclined to the left. The minimum birefringence occurs at a lower index of refraction than that found by the Becke method. There is a residual birefringence of about 0.004 (comparable to that of tridymite, dahllite, etc.). In relation to Wiener's theory we may say that, 1) there is a positive birefringence due to configuration (form) and, 2) there is a small residual birefringence.

Positive birefringence due to configuration of elements may be due to rod-shaped elements or to lamellae, both arranged parallel to the longitudinal axis of the fiber. In the first instance the birefringence $n_a - n_o$ is related to the indices of the rods and imbedding medium as follows:

$$n_a^2 - n_o^2 = \frac{\delta_1 \delta_2 (n_1^2 - n_2^2)^2}{(\delta_1 + 1) n_2^2 + \delta_2 n_1^2}$$

in which δ_1 and δ_2 are the volume elements of the rod and embedding medium ($\delta_1 + \delta_2 = 1$). The curve is asymetric in relation to n_2 and n_1. If we plot the value of $n_a^2 - n_o^2$ for various values of δ_1 and n_2, assuming $n_1 = 1.53$ we obtain a series of hyperbolae, in which the symmetry axis is always inclined to the right. Obviously our curve does not correspond to a system possessing bacillary birefringence.

The lamellary birefringence follows the relation

$$n_a^2 - n_o^2 = \frac{\delta_1\,\delta_2\,(n_1^2 - n_2^2)^2}{\delta_1\,n_2^2 + \delta_2\,n_1^2}$$

The relation is symmetrical in n_1 and n_2; moreover, for small values of δ_1 we find that the curve may be represented by a hyperbola the axis of which is inclined towards the left, as in our experimental curve. Because the expression is symmetrical in n_1 and n_2 it is immaterial whether the solid lamellae preponderate or whether the imbibition medium occupies most of the space in the cell wall. As soon as δ_1 is less than 0.1 the curve approaches in *shape* to our experimentally obtained one. Now it may be observed that in any mounting medium, the fibers remain dark between crossed nicols in transverse section. (comp. Fig. 6)

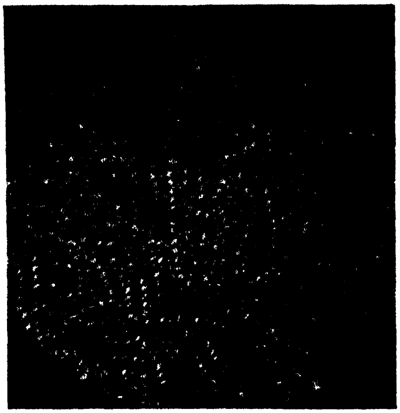

FIG. 6
Cross-section of genicular fibers of *Amphiroa dorbigniana* Decaisne photographed under crossed nicols. × 600.

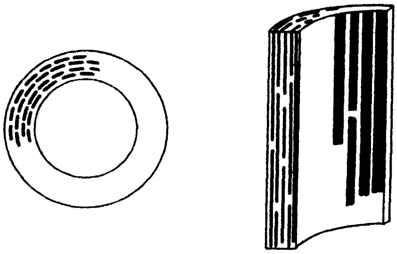

FIG. 7
Diagrammatic sketch of structure of a fiber. Not to scale.

If we suppose the lamellae to be arranged in tangential fashion parallel to length of fiber (Fig. 7), we would expect, when viewing the preparation in longitudinal section, to obtain birefringence in the wall, and a plotting of such should follow the equation for "Plättchendoppelbrechung" given by Ambronn-Frey,[2] page 119*; nγ should likewise be oriented parallel to the length of the lamellae. Viewed in cross-section, however, we expect to find a condition of isotropy, inasmuch as an entirely closed system (that is, a completely circular system) would produce no birefringence as depicted by Ambronn-Frey, page 122. It seems, then, that lamellae in tangential arrangement will fit the observed facts, and this arrangement is shown diagrammatically in the accompanying figure (Fig. 7). A critical examination of the other possible arrangements shows that the observed conditions could not possibly be fulfilled.

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*There is a typographical error here, as the equation should read

$$n_a^2 - n_o^2 = -\frac{\delta_1\delta_2\,(n_1^2 - n_2^2)^2}{\delta_1 n_2^2 + \delta_2 n_1^2}$$

In view of the water content of the fiber, which is difficult to determine experimentally, but in any case smaller than 90 per cent, we are inclined to believe that the fiber is built up of tangentially arranged elongate lamellae of pectin-like material, interspersed with concentric interstices. The pectin phase and the interstices are both small in relation to the wavelength of light, but the interstices occupy roughly less than one tenth the volume of the fiber.

The minimum in our curve at 0.004 may be interpreted in two ways. Krausse,[13] in his study on the structure of fibrous alumina obtained a curve of the same general shape as ours and with a minimum retardation of low value. He mentions the two possibilities, which we may apply to our case (page 288): "die Tonerdefasern sind aus länglichen Teilchen aufgebaut, deren Grösse und Entfernung von einander klein sind gegen die Wellenlänge des Lichtes. Diese Teilchen sind entweder isotrop oder positiv doppelbrechend in bezug auf ihre Längsrichtung."

X-ray photograms of powdered fibrous alumina as well as of our algal material seemed to indicate amorphic material.

The non-coincidence of the calculated and observed minima in our curve, as well as the curious retardations observed in various wavelengths may be explained by anomalous dispersion. It is well known that even small differences in light absorption for various wavelengths may cause a great difference in the refractive index. While the spectroscope revealed no such absorption bands in the coralline material, the cells, on visual inspection, are faintly but unmistakably yellowish.

As yet we have no conclusive evidence showing that the individual elements are, in themselves, birefringent. It would be rather like stressing the point to call these elements micellae. For they might as well run the whole length of the fiber. We meet here with the same difficulty that follows from Sponsler's[23] work on the fine structure of cellulose. Any division of the molecular chains is arbitrary. We cannot say, therefore, that our findings point to a micellar structure. (See, however, McNally & Sheppard,[14]) An elementary application of analytical geometry will convince us that the curve, experimentally obtained, actually represents a case of lamellary birefringence.

The expressions

$$Y = -\frac{\delta_1 \delta_2 (c - x)^2}{\delta_1 x + \delta_2 c} \tag{1}$$

and

$$Y = +\frac{\delta_1 \delta_2 (c - x)^2}{(\delta_1 + 1) x + \delta_2 c} \tag{2}$$

represent hyperbolae of the general form

$$Y = a + b x + \frac{c}{x + d} \tag{3}$$

the Y^2 term being absent. In this expression, the asymptotes are represented by $Y = a x + b$ and by $x = d$ respectively. The latter asymptote is therefore parallel to the ordinate axis.

The simple hyperbola $\frac{Y^2}{b^2} - \frac{a^2}{x^2} = 1$ transforms by rotation and translation of its axis into a hyperbola with one asymptote parallel to the ordinate if we rotate over $\alpha = \pm \text{arc tg} \frac{b}{a.}$ The general translation being $y = q, x = p$.

For a counterclockwise rotation $(-\alpha)$ we obtain

$$Y = -\frac{1 + tg^2\alpha}{2tg\alpha} x + \frac{1 + tg^2\alpha}{2tg\alpha} p + q - \frac{ab}{2} \frac{1 + tg^2\alpha}{1 - tg^2\alpha} \frac{1}{x - p} \quad (4)$$

and for a clockwise rotation $(+\alpha)$

$$Y = \frac{tg^2\,\alpha - 1}{2\,tg\alpha} x - \frac{tg^2\,\alpha - 1}{2\,tg\alpha} p + q + \frac{ab}{2} \frac{1}{x - p} \quad (5)$$

When we bring expressions (1) and (2) in the generalized form (3) we get; For lamellary birefringence

$$Y = -\delta_2 x + \frac{1 - \delta_1{}^2}{\delta_1} c - \frac{1 - \delta_1}{\delta_1{}^2} c^2 \frac{1}{x + \frac{1 - \delta_1}{\delta_1} c} \quad (6)$$

For bacillary birefringence

$$Y = \frac{\delta_1\,\delta_2}{\delta_1 + 1} x - \frac{2\delta_1\,\delta_2 \overline{\overset{\delta_1\,\delta_2{}^2}{\delta_1 + 1}}}{\delta_1 + 1} + \frac{\delta_1\,(1 - \delta_1)\,2 - \delta_1)\,(3 + \delta_1)}{(\delta_1 + 1)^3} \frac{1}{x + \frac{\delta_2}{\delta_1 + 1} c} \quad (7)$$

Equations (1), (4) and (6) correspond to the general expression

$$Y = -ax \pm b \pm \frac{c}{x \pm d} \text{ asymptote } Y = -ax \pm b$$

In this case the axis of the hyperbola is inclined to the left.
(lamellary birefringence)
Equations (2), (5) and (7) correspond to the general expression

$$Y = +ax \pm b \pm \frac{c}{x \pm d} \text{ asymptote } Y = +ax \pm b$$

The axis of the hyperbola is inclined to the right (bacillary birefringence). The curve obtained in this investigation may be interpreted as an expression of lamellary birefringence.

5. The Nature of the Mineral Deposition

Examination of thin sections of undecalcified Corallines show strong birefringence. In these sections we have been able to observe very small crystals oriented with n_α perpendicular to the cell wall. Their size was just about at the limit of the resolving power at aperture of 1.4. This would bring their length to a few tenths of a micron. Several attempts were made to ascertain the mineralogical nature of the crystals. We found that Meigen's reaction and the ferrous sulphate reaction were in conflict (compare also Johnston, Merwin, and Williamson.[12] These reactions have been shown to be unreliable. Direct inspection of the individual elements was impossible because of their size. Separations by specific gravity failed because of the small size of the crystals as well as their tendency to adhere to cellular fragments. Prolonged grinding in an agate mortar and grinding for forty eight hours in a ball mill failed to separate the individual crystals. n_ϵ and n_ω could not be determined, but inasmuch as no index of the calcareous material exceeded 1.633, it is reasonable to assume that the carbonate material is calcite. (Highest index of aragonite 1.685, dolomite 1.698, magnesite 1.700). This was already claimed by Meigen[15] who found no aragonite but only calcite in the Corallines, while the incrustated *Chlorophyceae* possessed aragonite. As his evidence was based upon color reactions of doubtful value, not much stress can be laid upon his confirmation. However, Dr. O. L. Sponsler had the kindness to prepare X-ray powder diagrams from both decalcified and natural *Amphiroa*. In measuring out his film Dr. Sponsler obtained identical results with Gibson, Wyckoff and Merwin[8] who worked with pure calcite. In the following table the first column represents the double angle from Gibson, Wyckoff and Merwin, Fig. 2, calcite; the second column represents Sponsler's results with powdered *Amphiroa;* the third column represents the quotients of the corresponding numbers in column B and A:

A Arc 2 θ (G,W,M)	B Arc 2 θ (O.L.S.)	$\frac{B}{A}$
12.3	28.0	2.28
16.0	35.7	2.23
19.5	43.5	2.23
21.3	47.5	2.23
23.4	52.0	2.23
25.5	56.7	2.21
26.2	57.5	2.20
30.1	67.5	2.24
32.3	71.5	2.21
34.5	76.0	2.20

The last column is constant within the experimental error. The incrusting material is, therefore, calcite with the c-axis oriented perpendicular to the cell wall. It may be said that the magnesium which is present in the deposit (Clarke and Wheeler[4]) might obscure the results. Our chemical analyses show that the magnesium content not only varies individually but that within the same organism it may fluctuate and may be zero in a great many cases. This is especially true in the younger parts of the plants which were sent to Dr. Sponsler for examination. Clarke and Wheeler[4] have repeatedly stressed the variability in the magnesium content of the Corallines. It is our belief that a comparative study of such forms as *Halimeda, Acetabularia,* which contain only small quantities of magnesium, and of the Corallines might lead to interesting results.

Summary and Conclusions

1. The cell-walls of the coralline algae are made of a non-cellulosic material; probably pectin or pectin-like substance.

2. The walls are birefringent in longitudinal- and isotropic in cross section.

3. The fibers are probably built up of tangentially arranged, elongate lamellae interspersed with concentrically arranged interstices, both of which are small in relation to the wavelength of light.

4. The only mineral that is deposited by the living Coralline is calcite. The individual calcite crystals are at most a few tenths of a micron long and are arranged with the c-axis perpendicular to the longitudinal axis of the fiber.

5. The deposition of magnesium in the corallines is a secondary phenomenon.

6. Our findings, while capable of being interpreted in accordance with the micellary hypothesis do not require this theory. The units in the cell wall are discrete, but not, within the cell, discontinuous.

Literature cited

[1] H. Ambronn: (1919) cited in Ambronn 1926.

[2] H. Ambronn and A. Frey: "Das Polarisationsmikroskop" (1926).

[3] M. Berek: Centralbl. Mineral. usw., **1913**, 388, 427, 464, 580.

[4] F. E. Clarke and W. C. Wheeler: The Inorganic Constituents of Marine Evertebrates. U. S. Geol. Survey, Prof. Paper, **124** (1922).

[5] V. v. Ebner: "Ueber die Ursachen der Anisotropie der organisierten Substanzen" (1882).

[6] A. Frey: Doppelbrechung der Dispersoide. Kolloidchem. Beihefte, **20**, 299 (1924).

[7] A. Frey: Die submikroskopische Struktur der Zellmembranen. Jahrb. Wiss. Bot., **65**, 195 (1926).

[8] R. E. Gibson, R. W. Wyckoff, and H. E. Merwin: Vaterite and Mu-Calcium Carbonate. Am. J. Sci., **10**, 325 (1925).

[9] T. Hashimoto and C. C. Wu: A simple laboratory quartz mercury lamp. Science, N. S. **65**, 187 (1927).

[10] G. C. Heringa and C. M. Minnaert: Concerning an Optic Phenomenon in Tendons. Proc. Roy. Acad. Amsterdam, **30**, 1 (1927).

[11] L. Irving and L. B. Becking: Observations on the Metabolism of the Corallines. Proc. Soc. Exp. Biol. and Med., **22**, 162 (1924).

[12] J. Johnston, H. E. Merwin, and E. D. Williamson: The several forms of calcium carbonate. Am. J. Sci., **41**, 473 (1916).

[13] W. Krausse: Zur Kenntnis des optischen Verhaltens der Tonerdefasern. Kolloidchem. Beihefte, **21**, 282 (1925).

[14] J. G. McNally and S. E. Sheppard: Double refraction in cellulose-acetate and nitrate films. J. Phys. Chem., **34**, 165 (1930).

[15] W. Meigen: Beitr. zur Kenntnis des kohlensauren Kalkes. Thesis. Freiburg (1902).

[16] A. Moehring: (1922) cited from Ambronn (2).

[17] H. Molisch: "Mikrochemie der Pflanzen" (1923).

[18] C. v. Naegeli: Beitr. zur wiss. Botanik, **1863**, Heft 3.

[19] C. Oltmanns: Morphologie und Biologie der Algen (1904).

[20] F. Pockels: "Lehrbuch der Kristalloptik", (1906). See, for more modern treatment of analogous matters: J. Errera: "Polarisation Diélectrique" (1928).

[21] W. J. Schmidt: "Die Bausteine des Tierkörpers in polarisiertem Lichte" (1924).

[22] Graf zu Solms-Laubach: "Die Corallinenalgen des Golfes von Neapel" (1881).

[23] O. L. Sponsler and W. H. Dore: The Structure of Ramie Cellulose as derived from X-ray Data. Colloid Symposium Monograph, **4**, 174 (1926).

[24] G. Valentin: Die Untersuchung der Pflanzen und der Tiergewebe in polarisiertem Lichte" (1861).

[25] O. Wiener: Die Theorie des Mischkörpers f. das Feld d. stationaren Stromung. Abh. Math. Phys. Kl. Sächs. Ges. der Wiss., **32**, 507 (1909).

[26] K. Yendo: Study of the genicula of Corallinae. J. Imp. Coll. Sci. Tokyo, **19**, (1904).

THE DISSOCIATION OF STRONG ELECTROLYTES. III*

Complete Dissociation and Optical Properties

BY MORRIS B. JACOBS AND CECIL V. KING

The supposed additivity of color or light absorption, of refraction and of dispersion by the ions in solutions of strong electrolytes has in recent years been cited in favor of complete dissociation, just as thirty years ago similar data were used to support the Arrhenius dissociation theory. The Arrhenius theory indicates that some properties of strong electrolytes should be found which can be assigned to the undissociated molecule; and the difficulty of specifically assigning any properties to such a portion of the electrolyte has recently been interpreted in favor of its complete absence.

Color and Absorption.—As far back as 1892 Ostwald[1] called attention to the fact that a solution of any electrolyte should show at least three absorption spectra—one for each ion and one for the undissociated molecule; if complexes were formed, the absorption spectrum would be even more complicated. Ostwald showed that thirteen different metal permanganates, at a dilution of one equivalent in 500 liters, had absorption bands in identical positions in the spectrum. Ten salts of fluorescein showed the edge of their absorption band in the same place, and eosin and anilin violet salts were similar in this respect. Ostwald took this, of course, to mean that these salts were highly dissociated in these dilute solutions, and that the metal ions and anions were highly independent; for the changing or substitution of atoms or radicals in non-conducting organic molecules is usually attended by pronounced color changes. Ostwald did not attempt to show evidence of absorption by the undissociated molecules of these salts.

Also in 1892 Magnanini showed that two solutions of copper sulfate of the same concentration, one containing considerable sulfuric acid, had exactly the same light absorption. He interpreted this as evidence against ionization, but Ostwald replied that undissociated $CuSO_4$ might well have the same absorption, in solution, as copper ion. Magnanini then (1893) proceeded to show that the addition of KNO_3 to potassium violurate did not change the absorption; he was under the impression that violuric acid and the violurate ion (if it existed) were not colored and that undissociated potassium violurate was the only colored substance present. Donnan[2] describes the above experiments and shows that Magnanini's work was marred by the impurity of his materials. Donnan himself shows that, assuming that the color is due to the violurate ion only, one can calculate the percentage ionization and the dissociation constant of violuric acid from the color at various dilutions, and obtain results identical with those from conductivity measurements. This is pointed out by Halban[1] who shows that $\mu/\mu_\infty = \epsilon/\epsilon_\infty = \alpha$ for this acid. (μ = equivalent conductivity, ϵ = extinction coefficient).

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* Contribution from the Department of Chemistry, Washington Square College, New York University.

[1] Ostwald: Z. physik. Chem., 9, 579 (1892).

[2] Donnan: Z. physik. Chem., 19, 465 (1896).

Bjerrum[2] found that the color, in solution, of certain chromium salts was practically constant on dilution, i.e., the molecular extinction coefficient did not change with the concentration; he interpreted this to indicate the absence of undissociated molecules. In 1918 Bjerrum[3] summarizes the evidence for complete dissociation and points to his earlier conclusion from the color of these chromium salts. He points out that α and i-1 (from conductivity and from colligative properties) do not agree and remarks that if these are abandoned as a measure of the degree of dissociation the "anomaly of strong electrolytes" disappears. He emphasizes that his conclusions from the color of salts apply *only when no complexes are formed.*

Noyes[4] on the basis of similar observations concluded that since the optical activity, color, etc. were independent of the concentration (when referred to equivalent quantities), these properties were additive with respect to the ions even at concentrations where much of the salt was un-ionized. At that time, in other words, Noyes interpreted constancy of color or absorption to mean that *ionization is an optically indifferent process*, and that the color is the same whether the ions are "bound" or "free", a view which has been held for many years by Hantzsch.[5] Hantzsch, like Bjerrum, found that many strong electrolytes show practically no change in molecular extinction coefficient on dilution. This was true for the Sr, Li, Na, Cs, Tl salts of acetyloxindon, for some copper salts and copper complexes in water, aqueous ammonia and other solvents, for permanganates, chloroplatinates, potassium diamminetetranitrocobalt, and for K and Ba salts of trichloroacetic acid (in ultra-violet light). Further, he showed that trichloroacetic acid has exactly the same absorption in *petroleum ether* as in water, and that HBr is optically identical in water, alcohol and ether; also that many salts show the same constancy of molecular absorption in alcohol solution as in water. Recently, with more exact experimental work, he shows that the ultraviolet absorption by various halides is not strictly additive, and ascribes the discrepancies to minor chemical changes such as hydration. Remembering that substitution in un-ionized organic compounds has often a pronounced effect on the color, and that ionization should be less in some of these non-aqueous solvents than in water, Hantzsch concludes that ionization is an optically indifferent process.

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[1] Halban: Z. Elektrochemie, **34**, 489 (1928).

[2] Bjerrum: Det Kgl. Dansk. Vid. Sel. Skr., (7) **4**, 26 (1906); Z. anorg. Chem., **63**, 140 (1909).

[3] Bjerrum: Z. Elektrochemie, **24**, 321 (1918).

[4] Noyes: Science, **20**, 577 (1904).

[5] Hantzsch and co-workers: Ber., **41**, 1216, 4328 (1908); **58**, 612 (1925); **59**, 1096 (1926); Z. physik. Chem., **63**, 367 (1908); **72**, 362 (1910); **84**, 321 (1913); **86**, 624 (1913); Z. Elektrochemie, **29**, 221, 434 (1923); **30**, 194 (1924); **31**, 167 (1925).

Hantzsch in this matter disagrees with Halban,[1] who has also done much experimental work on absorption by strong and weak electrolytes.

Halban at first agreed with Bjerrum's view, and not Hantzsch's; since Beer's law is obeyed by strong electrolytes and not by weak ones, ionization cannot be an optically indifferent process. He even showed, as has been mentioned, that the percent ionization of a weak electrolyte might be calculated from the extinction coefficients. Later, however, Halban came to the conclusion that Beer's law is by no means generally valid even for strong electrolytes; he points out that the salts cited by these workers were mostly rather complex salts, while the relation is not obeyed by some of the simplest salts. For instance, while for the complex chromium salts ϵ is practically constant with concentration while μ is not, for the absorption in the ultraviolet by lithium nitrate ϵ follows much the same type of curve as μ. Also, while according to Bjerrum's idea addition of another salt should have no effect on the absorption by the first, actually enormous effects may be observed.

Halban, while assuming practically complete dissociation in such cases, explains the invalidity of Beer's law according to the electron-shell deformation theory of Fajans.[2]

Halban and Ebert, in a careful piece of experimental work, show with exact measurements that Beer's law is not strictly valid for several strong electrolytes and that the absorption of various salts is influenced greatly by the addition of non-absorbing salts.

Halban and Fajans both admit the possibility of hydration or of equilibria which may include undissociated electrolyte or groups of ions of both signs in equivalent or non-equivalent amounts. Fajans[3] admits the necessity of this since neither the molecular absorption or refraction is strictly additive for many strong electrolytes. Part of the discrepancy, he decides, is due to ion deformation; but this does not account for all the variations and the presence of molecules, ion groups or complex ions is indicated.

In many cases color changes are apparently connected with changes in the degree of hydration of the salt. The molecular absorption of cobalt chloride in water and various alcohols[4] was found not to be constant with changing concentration, but to increase, decrease, or pass through a minimum as the dilution progresses. The gradual change in color in passing from a dilute to saturated aqueous solution and then to alcoholic solutions is perhaps best explained by a change in the degree of hydration of the salt.

E. F. George[5] found the absorption of light by certain electrolytes to change with concentration, to be presumably a function of their state of dissociation, and to be influenced by the addition of salts having a common ion.

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[1] Halban: Z. Elektrochemie, **29**, 434 (1923); **30**, 601 (1924); **34**, 489 (1928); Halban and Ebert: Z. physik. Chem., **112**, 321 (1924).

[2] Fajans: Naturwissenschaften, **11**, 165 (1923). Also other papers by Fajans and coworkers.

[3] Z. physik. Chem., A **137**, 361 (1928).

[4] Hulbert, Hutchinson and Jones: J. Phys. Chem., **21**, 150 (1917).

[5] George: Dissertation, Ohio State (1920).

Hüttig and Keller[1] found that exact measurements showed the molecular absorption in the ultraviolet of all the halides of lithium to change with concentration.

Houstoun and his coworkers[2] studied the absorption of many salts in aqueous and non-aqueous solutions; mostly salts which show extensive hydrate and complex ion formation, as ferric, nickel, cobalt, and copper halides. With these salts no constancy of extinction coefficient with concentration is found; no additivity of absorption for anion and cation. Houstoun reaches the conclusion that solvation plays an important role in the color of ions; and that in dilute solutions where additivity is to be expected, the spectrophotometric methods in use at that time were inadequate to prove constancy of molecular absorption.

Very often the factor of complex ion formation and its effect on color have been neglected. Bjerrum repeatedly emphasizes that absorption may be additive for the ions and one can expect this to mean complete dissociation *only when no complexes are formed.* Considerable work has also been done to show a parallelism between color change and complex formation in certain cases.[3]

From the above can be seen the difficulties involved in using color or light absorption in support of the theory of complete dissociation. The possibility of complex ion formation even in dilute solution limits the application of this theory considerably.[4] For color and absorption data to be entirely satisfactory evidence of complete dissociation, Beer's law should hold unqualifiedly for strong electrolytes, and color and absorption should be strictly additive for anion and cation; but these conditions are met only with good approximation in some cases and not at all in others. Hence one can adopt any of several views:

(1) The older view of Noyes: that undissociated molecules of strong electrolytes are potentially ionized and dissociation of these ions is an optically indifferent process;

(2) The view of Hantzsch: that ionization itself is an optically indifferent process, and change in color is connected, rather, with a change in chemical constitution;

(3) The view of Bjerrum: that ionization is not an optically indifferent process and that validity of Beer's law indicates complete dissociation (minor divergences being explained by Bjerrum's ion-association theory or other factors);

(4) The view of Halban and Fajans: that ionization is not an optically indifferent process, that even large departures from additivity or from Beer's

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[1] Hüttig and Keller: Z. Elektrochemie, **31**, 390 (1925).

[2] Physik. Z., **14**, 424 (1913); Proc. Roy. Soc. Edinburgh, **33**, 35, 44, 137, 147, 156 (1913).

[3] For example—Denham: Z. physik. Chem., **65**, 641 (1909); Mecke and Ley: **111**, 385 (1924); Ley and Heidbrink: Z. anorg. allgem. Chem., **173**, 287 (1928); Getman: J. Phys. Chem., **26**, 377 (1922).

[4] See also McBain and Rysselberge: J. Am. Chem. Soc., **50**, 3009 (1928); **52**, 2336 (1930). See, however, Freed and Kasper: J. Am. Chem. Soc., **52**, 2632 (1930).

law can be explained by the ion-shell deformation theory, and that some small percent of the electrolyte may be in the form of groups of ions or even neutral molecules;

or (5) The view that we wish to emphasize here, namely that the percent dissociation can no more be calculated with certainty from color or absorption data than from α $(=\mu/\mu_\infty)$ or i-1.

Refractive Index.—The above statements apply almost verbatim to the supposed additivity of refraction by the ions. The smallness of change in molecular refractivity with concentration has often been cited in support of complete dissociation. Thus Bjerrum[1] commented on the work of Fajans. Fajans answered that if such small changes are real, they must be significant. When the Arrhenius theory was first presented, the approximate additivity of refractive index was used as a support for the theory; now it is used as evidence of complete dissociation, and the discrepancies are explained by ion association, deformation, hydration, complex formation, etc. It will be seen that almost every experimenter has his own explanation for the small or great divergences from true additivity.

Additivity of refractive index has been cited as evidence of complete dissociation by Lewis[2] in his famous address "The Use and Abuse of the Ionic Theory"; by Lewis and Randall[3]; by Lange,[4] who says the existence of appreciable numbers of molecules in solutions of strong electrolytes has not yet been provided by optical (or other) means; by Harned[5] who says "The additivity of the refractive indices, rotatory powers . . . is well known"; etc.

With refractivity we have the same difficulty in explaining the experimental data as with optical rotation and light absorption. Actually the molecular refraction is usually not additive for the solid electrolyte and the solvent; and sometimes the calculated molar refraction of the solute remains nearly constant with change of concentration, sometimes it does not. If it does remain nearly constant, we can interpret this fact in two ways: (1) the electrolyte is completely dissociated at all concentrations; or (2) the electrolyte has very nearly the same refractive power whether ionized or not. If the refraction does not remain constant, we can interpret this fact in two ways: (1) the electrolyte is completely dissociated, and the change in refraction is caused by ion association, ion deformation, or some other factor; or (2) the ions and the molecules have widely different refractive powers.

Walden[6] measured the molar refractivity of tetramethylammonium iodide, tetrapropylammonium iodide, and phenylethyldimethylammonium iodide in water and in a series of other solvents of high and low dielectric constants. He found only 1 or 2 percent change over a wide concentration range in most of the solvents; also a rather small difference in solvents of high and low dielectric constants. It is hard to see how these results can be interpreted in favor of complete dissociation in aqueous solution; if the salts are really unionized in the non-aqueous solvents of low dielectric constant, then the molecular form has nearly the same refractive power as the ionized form.

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[1] Trans. Faraday Soc., **23**, 376 (1927).

[2] G. N. Lewis: Z. physik. Chem., **70**, 212 (1909).

[3] Lewis and Randall: J. Am. Chem. Soc., **43**, 1112 (1921); "Thermodynamics", 318, 319 (1923).

[4] Lange: Physik. Z., **29**, 760 (1928).

[5] Taylor's "Treatise of Physical Chemistry", **2**, 790 (1925).

[6] Walden: Z. physik. Chem., **59**, 385 (1907).

H. C. Jones and his coworkers[1] carried out many experimental studies on the refractive index of salt solutions. They found that, in general, the refractivity of the electrolyte was proportional to its concentration. In many cases the refractivity of the pure electrolyte could be predicted from the study of its solutions; they concluded that when this could not be done, the electrolyte formed hydrates in solution.

Rimbach and Wintgen[2] used the refractive index to determine the formation of complexes in solution. They found the refraction to be additive for pairs of salts which form no complexes, as NaCl-KCl, $AgNO_3$-$LiNO_3$ etc. Likewise the refraction was additive for the components of mixtures which deposit double salts, as alums, which led to the conclusion that these double salts are completely dissociated in dilute solution. Mixtures of salts which are known to form complexes, as $CdCl_2$-KCN, $AgNO_3$-KCN, gave entirely different results, the refraction being not at all additive. Thus, they say, measurements of refractive index can be used to give qualitative knowledge of complex formation; but the change in refractive index is too small for quantitative work (usually not over 1% even for concentrated solutions).

Schwers[3] shows that the ratio of change of density to change of refraction with change in concentration, for sulfuric acid, increases with the dilution. From a study of this coefficient he concludes that in many cases—HCl, HBr, HI, H_2SO_4—the refractive index change, for the same specific volume change, is less in dilute than in concentrated solution; or in other words, that ionization (assuming the Arrhenius theory) lowers the refractive index (at constant density). Schwers points out that LeBlanc came to the opposite conclusion, i.e., that the ions have a greater refractive power than the molecules. Other authors reached the conclusion that the ions and molecules have the same refractive power; in other words, that ionization is an optically indifferent process.

Chéveneau[4] made careful determinations of the refractive indices of solutions of KCl, NH_4NO_3 and $Mg(NO_3)_2$. He found practical constancy of specific refraction of the electrolyte over a considerable concentration range, but in very dilute solutions there was a pronounced increase or decrease. In 1910 he indicated the possibility that this was due to lack of adequate temperature control; but in 1921 the experiments were repeated with all precautions for keeping the temperature constant and the previous results were completely verified. Chéveneau interpreted these results to indicate that ionization has no appreciable influence on the specific refractive power in solutions of concentration over ½ gram per liter; the changes at higher dilution he attempts to explain on the basis of a change in vibration frequency of the constituents of the electrolyte, and compares the dissolved substance in dilute solution with an attenuated gas.

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[1] Many papers in Am. Chem. J.; Z. Elektrochemie; Z. physik. Chem.; Carnegie Institution Publications; etc.

[2] Z. physik. Chem., **74**, 233 (1910).

[3] Z. physik. Chem., **75**, 621 (1911).

[4] Compt. rendu, **150**, 866 (1910); **172**, 1408 (1921).

It can be seen that the earlier work on refraction by electrolytes in solution by no means gave the conclusive proof of additivity that the exponents of complete dissociation would have one believe. The difficulty of exact enough measurements, the uncertainty of calculation of the molar refractive power of the dissolved electrolyte, the lack of knowledge concerning formation of hydrates and complex ions all contributed to the uncertainty regarding the interpretation of refractive index data. The most accurate experimental work done prior to 1920 could scarcely distinguish between complete or 95% ionization, even if other complicating factors were absent. This was the status of the problem until the work of Debye and Hückel stimulated further research.

Fajans and his coworkers[1] have done much experimental work on refractive index with the express intention of learning the condition of strong electrolytes in aqueous solution. They point out that very few of the older measurements are sufficiently accurate to test rigorously additivity of refractive power of the ions; and show the difficulty of calculating the true refractivity of the solute in those cases where the refractivity of solvent and solute are not additive. The molar refractivity of sulfuric acid, Fajans says, is constant up to a concentration of 30%; this is, however, by no means true for HCl and many salts. For many salts the refraction extrapolated to infinite dilution is additive for the ions, but this is not true at finite dilution. The equivalent refraction of most salts shows a linear relationship with the concentration. Fajans concludes from refractometric and other optical data and from vapor pressures, that in solutions of strong electrolytes ion deformation plays an important role but that there are undoubtedly some neutral molecules or at least pairs of ions and complexes perhaps of the type H_2Cl^+. He points out emphatically that we have every gradation from the strongest to the weakest electrolytes. Strong electrolytes differ from weak electrolytes only in degree; the essential modification of the classical theory lies in taking account of the inter-ionic forces in any quantitative treatment of the subject.

The refractive index of the halides of lithium was measured by Hüttig and Keller:[2] it was found that the refractivity of the salts and the water was not additive, and the value for the salts varies with the dilution. Fajans remarked that the refraction of the solution was in all cases greater than the sum of that of the salt and the water, indicating greater ion deformation, the closer the salt atoms. Hüttig ascribed the effect to hydration, whether in conjunction with ion deformation or not.

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[1] Z. Physik, **23**, 1 (1924); Ber., **59**, 249 (1926); Trans. Faraday Soc., **23**, 357, 375, 408 (1927); Z. physik. Chem., **130**, 724 (1927); A **137**, 361; B **1**, 427 (1928); Z. Elektrochemie, **34**, 1 (1928).

[2] Z. Elektrochemie, **31**, 390 (1925).

Conclusions.—We can only conclude from the above that the "additivity of optical properties" is a myth; true in some accidental cases, nearly enough true in others so that the discrepancies were not noticeable in the older measurements or could be overlooked. Closer examination shows that from the very nature of the properties under consideration, since the experimental variations are so small, the older, less exact work could be interpreted in favor of the Arrhenius theory as well as the complete dissociation theory. In either case the most exact recent work shows that there are discrepancies to be explained by some other means than the degree of ionization. The observations considered here, in connection with the other experimental evidence, undoubtedly indicate that the conductivity ratio gives values too small for the degree of ionization; but there is mounting evidence of the existence of some small percent of undissociated molecules, or ion-pairs or groups, in even the best examples of highly dissociated electrolytes. Too many workers forget that the inter-ionic attraction theory does not require complete ionization. And it must be remembered that at the high dilutions where there seems to be fair agreement with the Debye-Hückel equations, even the Arrhenius theory postulates nearly complete dissociation.

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THE CHEMISTRY OF TURKEY-RED DYEING

BY LYTLE RAYMOND PARKS

Introduction

Knecht, Rawson and Loewenthal[1] discuss "Turkey-red" in general as follows: "The art of producing a fiery and permanent red on cotton with the aid of madder roots, fatty oils (buffalo's milk or sheep's milk), and aluminium salts was known in the East Indies centuries ago, from whence it spread westward through Persia, Armenia, and Syria to Turkey and Greece. Since the middle of the eighteenth century the art of dyeing this brilliant red was brought by the Greek dyers to Rouen, Lyons, and Languedoc in France, where several "Turkey-red" dye works were founded. In 1765 a pamphlet, written by d'Apligny, was published by the French government, in which full instructions are given for producing Turkey-red. As a result of this publication the process became widely known and employed in Western Europe. The first Turkey-red dye works in Great Britain were probably founded in Glasgow in the year 1790, in which district (Vale of Leven) the Turkey-red dyeing industry of that country is still chiefly located; Turkey-red is dyed also in large quantities in the vicinity of Mulhouse (Alsatia), Elberfeld-Barmen (Prussia), and elsewhere. In Western Europe Turkey-red was at first exclusively dyed on cotton yarn; but in 1810 Koechlin of Mulhouse introduced it as a dye for woven fabrics.

"The process as it came from the East was very lengthy, requiring as much as four months; but the time was much shortened prior to the discovery of Alizarin, some 125 years later; and now Turkey-red can be produced in three days which is as fast to light as the colour obtained by the long process. No difference exists between the fastness of the red dyed with madder or with Alizarin. But the colour obtained by the long process is more resistant to chlorine, and slightly clearer than the red produced quickly with the aid of Turkey-red oil, probably on account of the incidental bleaching of the fiber by the sun during the prolonged and frequent exposure in fields after the repeated oiling operations; and there are dyers in various parts of the world who still use the old method and obtain for the products correspondingly higher prices; but those form a very small part of the Turkey-red produced.

"During the last quarter of the nineteenth century a revolution in Turkey-red dyeing has been caused by the substitution of Alizarin for madder, and by the introduction of new methods of oiling. Dyers willingly accepted the artificial dyestuff, since it was well adapted for application by the long established dyeing process; but weavers at first complained that the yarns were too greasy and could not be sized well. Dyers, however, soon recognised the fact that the artificial dyestuff did not require such severe cleaning with soap and soda as the natural products, and that the amount of oil in the preparation of the yarns could be diminished; thus this drawback was rapidly overcome, and as early as 1873 Alizarin had completely displaced madder in some of the principal dye-works of Switzerland, notwithstanding the high price at which Alizarin was then sold. This was principally due to the brighter shades that could be obtained and the shortening of the process of oiling and brightening.

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[1] **Knecht: "A Manual of Dyeing" 2, 579 (1910).**

"In the old process lukewarm rancid olive oil is used. Under the name of "Steiner's process" a much shorter method of oiling the goods with very hot olive oil came into use. But olive oil has been replaced in most dye-houses altogether by new preparations of castor oil (or of olive oil), the so-called Turkey-red oils, with the aid of which products the oiling operations could be reduced in number and in time without too great a loss in fastness. Thus fine shades of New Turkey-red are obtained at relatively low prices and in a short time, which are exceedingly fast to light and soap, although inferior to the red obtained by the emulsion process. Finally, we may mention various processes of dyeing a red on cotton with the aid of Alizarin and aluminium mordant without any previous oiling of the goods, although an oiling follows the dyeing. These shades are not considered to be Turkey-reds; they are called Alizarin reds and are inferior in fastness and brilliancy to Turkey-red; still they belong to the fastest colours produced and are dyed in very great quantities, especially on cotton goods.

"Turkey-red, as produced on the fibre, is a very complicated compound, the basis of which probably is the calcium aluminium lake $(C_{14}H_6O_4)_3Al_2$, CaO,H_2O, described by Liechti and Suida. The following series of operations serves for the production of Turkey-red:—

(1) Oiling with a fatty oil (olive oil, castor oil, or Turkey-red oil).
(2) Sumaching.
(3) Mordanting or Aluming.
(4) Dyeing.
(5) Clearing.

"A considerable number of washings is absolutely necessary between these processes in order to obtain anything like a good red colour; but the formation of the colour itself is independent of these.

"(1a) Oiling with Olive Oil. —Oils of vegetable origin are exclusively used, olive oil being superior to all others. (In the East Indies the crushed castor oil seeds are used). The best kind of olive oil for this purpose is the rancid Gallipoli oil or emulsion oil (French, huile tournante) which has become rancid by the nitrogenous and extractive matter which it contains. It contains, owing to partial decomposition, more or less free fatty acids (oleic acid and others) as also free glycerin. This oil forms a milky emulsion with sodium carbonate, which emulsion may be partly a solution, and partly a mixture of the finely divided undecomposed oil with the soap (formed by the free acid and sodium carbonate), free acid and possibly glycerin. This emulsified oil is absorbed by the fibre with special facility. The process of oiling consists in steeping the cotton material (yarn or piece goods) in the emulsion, and subsequently exposing the fibre with the oil to the action of the open air (ageing), or (in Steiner's process) to an elevated temperature in ageing rooms. To increase the quantity of oil thus deposited and transformed in the fibre the oiling and exposing process is repeated several times.

"By the exposure the oil is rendered insoluble so as to adhere permanently to the fibre. The chemical reaction effecting this change probably consists in a further decomposition of the olive oil into free acids and glycerin and in an oxidation and polymerisation of the liberated oleic acid under the influence of air, light, heat, moisture, and sodium carbonate. This has not been well established, but it is well known that oleic acid is very oxidisable and disposed to polymerise; according to Camille Koechlin, 1 part of oleic acid absorbs 300 to 400 parts (by volume) of oxygen under the influence of light. The fact that when recently oiled goods are piled up in heaps without being aired by turning, the temperature rises considerably, and may even reach spontaneous ignition, appears to favor the view that an oxidation takes place.

"From the fibre which has been prepared and well washed, a substance can be extracted by solvents which does not contain glycerin, part of which gives a soap with barium hydroxide, while another part is neutral and cannot be saponified. These compounds are probably the products of oxidation and polymerisation of oleic acid and possibly of the other components and admixtures of olive oil. The fibres which have been deprived of these substances do not yield a serviceable red with Alizarin, but a fair colour is obtained when cotton is impregnated with the extract and subsequently mordanted with alumina and dyed with Alizarin.

"The oil as fixed in the fibres has probably a double effect:

(i.) It combines with and helps to fix the metallic mordant, as in the case of Turkey-red with aluminium and calcium, and in the very similar case of violet with iron and calcium;

(ii.) It forms a colorless transparent varnish around the colour lake which protects the same from the influence of light, air, and chemical agencies, and, at the same time, increases the lustre and fastness of the shade. It may be assumed that in the more rapid processes of preparing the cotton sufficient time is not given for the formation of this varnish like substance; this would account for the inferior fastness of such kinds of Turkey-red.

"(1b) Oiling with Turkey-red Oil.—The use of an olive oil which had been treated with sulphuric acid, as is now the case in the manufacture of Turkey-red oil, was recommended as early as 1834 by Runge in his work, Farbenchemie (Chemistry of Colours). During the seventies of last century Fritz Storck and Dr. Wuth discovered, almost at the same time, the preparation of Turkey-red oil from castor oil, and by its use greatly simplified the process of Turkey-red dyeing.

"The nature of Turkey-red oil has been discussed in Part V, and it has been stated that it contains compounds of certain organic acids with the radical of sulphuric acid, which represent either a sulphate (ester) or a sulphonic acid of ricinoleic acid. These compounds are rapidly decomposed under the influence of ageing and steaming, the sulphuric acid being separated from the organic acids and the latter being transformed into substances similar to those produced by the preparation of cotton with emulsive oil. The advantage of the Turkey-red oil over the emulsive oil is that it can be fixed in a short time by ageing, thereby allowing the laborious and lengthy exposure to the air to be dispensed with.

"The cotton which has been prepared with oil (by either method) is now treated with warm water and then with caustic soda (steeping). By this operation the fibre is purified, while the oil which has been fixed on the material is not affected.

"(2) Sumaching.—The cotton is usually saturated with a decoction of sumach after it has been impregnated with the oil. The object of this process is to introduce tannic acid into the fibre so as to render it capable of fixing, during the subsequent "aluming" operation, a larger quantity of alumina and of ultimately acquiring a fuller colour. It is uncertain whether the tannic acid enters into the ultimate colour lake or whether it forms a separate lake with the alizarate of aluminium and calcium. The sumaching operation is not absolutely necessary, since there is no decrease of fastness or of brilliancy of colour and no alteration of the shade if it is dispensed with. The sumaching, however, is considered by some dyers to give the colour a greater resistance towards the action of chlorine.

"(3) Aluming.—By the process of mordanting with aluminium salts, one of the metallic mordants which is required for the formation of the red colour lake—namely, aluminium—is incorporated with the material. It is permanently fixed by the subsequent operation of ageing, washing, and chalking, while the acid of the aluminium salt is removed. Calcium, the other metallic mordant, need not be introduced into the fibre before dyeing.

"Sometimes a small amount of stannous chloride or, better, stannous acetate is added to the mordanting bath to produce a more fiery shade; but what part the tin has in the formation of the colour lake is unknown. Some add the tin salt to the dye bath or to the second clearing bath; but nothing definite can be said as to its mode of action.

"(4) Dyeing.—The mordanted material is dyed in a bath which has been prepared with the required amount of Alizarin, and which must also contain a certain amount of lime salt to form the colour lake. If the water has great temporary hardness, it contains the required amount of lime salt in the form of calcium bicarbonate; but if it is very soft, some chalk or calcium acetate must be added. It has been shown by Liechti and Suida that Alizarin and aluminium do not combine in the absence of calcium compounds; but the addition of a calcium salt causes the rapid formation of a lake, which is probably constituted according to the formula $(C_{14}H_6O_4)_3\,Al_2 . CaO . H_2O$. Sometimes a stannous salt is added to the dye-bath, which may have the double effect of producing an Alizarin-tin lake and of reducing ferric oxide, thereby preventing the latter from forming part of the colour lake; the ferric oxide, which is easily introduced into the dye-liquor as an impurity, has a very dulling effect on Alizarin-red shades.

"Alizarin and calcium are taken up by the fibre from the dye-bath; but the lake is not completely formed until the temperature is raised above 70°; if the goods have been dyed at a lower temperature, as is the case in the sulphated oil process, they possess a reddish-orange colour when they are taken from the bath, and the red is developed by steaming only, which process completes the long chain of operations required for the formation of the colour-lake, provided that in the second clearing bath no further change is effected.

"(5) Clearing.—The dyed goods are treated twice with hot solutions of soap. The first soaping merely removes a great amount of impurities which become attached to the fibre during the lengthy operations of oiling, mordanting, and dyeing. The utility of the addition of stannous chloride to the second soap bath is disputed. This salt makes the soap solution more neutral, sodium chloride and stannous soap being formed. Possibly the stannous salt exerts a reducing action on the ferric compounds which may have been taken up during the process and which would dull the shade, while the stannic oxide thereby formed enters the colour lake and renders the shade brighter and more fiery. It is contended, however, that stannous chloride cannot act in this way when added to the clearing bath, as the colour lake has already been formed, and that it should therefore be added to the mordanting liquor or to the dye-bath. According to another view, which is supported by Liechti's researches, a tin oleate is produced by the action of stannous chloride in the clearing bath, and is spread as a varnish over the fiber without entering into combination with the colour lake itself. Liechti has shown that 60 percent of the fatty acid of the soap employed may disappear and become fixed to the fibre."

The above-described process is so involved that we marvel at the results obtained, and especially at the ingenuity displayed in devising the original method and the modifications which followed. However by considering Turkey-red dyeing from the standpoint of Bancroft's Theory of Dyeing[1] and Mordants[2] the mystery disappears and the process stands out as comparatively simple.

According to the above-mentioned theory, dyeing consists in imparting a moderately fast color to a substance as the result of immersing it in a suitable, true or colloidal, solution called a dye-bath. Such a solution usually contains a colored substance dissolved or peptized but may contain a substance which can be converted into a colored material. Thus the indigo vat is not blue. The vat is yellow and contains reduced indigo (indigo white), the blue color appearing after the indigo white is oxidized on the cloth. In most cases the coloring matter is adsorbed by the substance dyed and does not form a chemical compound with it.

A mordant is considered as a substance which is strongly adsorbed by the fibre and which itself adsorbs the dye strongly.

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[1] Bancroft: J. Phys. Chem., 19, 50, 145 (1915).

[2] Bancroft: J. Phys. Chem., 26, 447, 501 (1922).

A study of the problem from the standpoint of the above-mentioned theory involves the consideration of five different things.

1. The relation of the metallic mordant to the fibre.
2. The relation of the fixing agent to the fibre.
3. The relation of the fixing agent to the metallic mordant.
4. The relation of the dye to the mordant.
5. The brightening of the color.

Procedure and Experimental Results

For these experiments unbleached muslin was converted into standard cellulose according to the method suggested by Leighton.[1] The cotton was heated for 18 hours on a water bath with a one percent solution of sodium hydroxide. It was washed with distilled water, then with dilute HCl and again with water until the wash was neutral to litmus, after which it was dried in an oven at 115° for six hours.

Taking up of Alumina by the Fiber.—A solution of aluminium acetate was prepared from aluminium sulfate and lead acetate in order to obtain the amount, if any, of alumina which was taken up by the cotton. 25 c.c. portions of this solution were precipitated by ammonium hydroxide, filtered, ignited, and weighed as Al_2O_3. The value found was 0.00466 grams Al_2O_3 per c.c. of solution. Two solutions were made up from this standard of known alumina content and a known weight of cotton placed in each and allowed to stand for 24 hours. 50 c.c. portions were then drawn off by means of a pipette and the alumina content determined as above described. The difference in the concentration before and after treatment with the cotton indicated the amount adsorbed. The following data show this to be very small.

Table I

Adsorption of Alumina by Cotton

g. cotton	g.Al_2O_3 used	g.Al_2O_3 found	g.Al_2O_3 adsorbed	total per 1 g. cotton
2.4444	0.1398	0.1385	0.0013	0.00053
2.1954	0.1864	0.1856	0.0008	0.00036

Adsorption of Sulphonated Oil by the Fiber.—Strips of wet cotton cloth were allowed to dry in the air, and then dried in an oven at 50°C for twenty-four hours. The strips were then placed in glass-stoppered weighing bottles and weighed. After weighing they were placed in solutions of Turkey-red oil of different concentrations and shaken for 18 hours at room temperature. The cloth was then removed from the solution and hung up to dry at room temperature without previously pressing out the oil. However the surplus oil could drain from the sample. After air-drying the samples were placed in an oven at 50°C for twenty-four hours and again weighed. The gain in weight represents the amount of oil adsorbed. While this method does not give absolute adsorption values, the results show relative adsorption. The experimental data is given in Table II and shown in graphic form in Fig. 1.

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[1] Leighton: J. Phys. Chem., **20**, 32 (1916).

An examination of Fig. 1; where C equals the grams of oil in the filtrate at equilibrium and x/m the grams of oil adsorbed by one gram of adsorbent; shows that a smooth curve is obtained, free from breaks, indicating the adsorption of Turkey-red oil by the cotton.

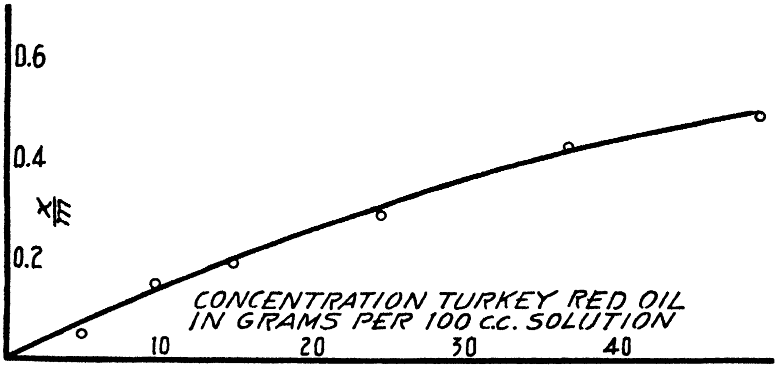

FIG. 1
Adsorption of Turkey Red Oil by Cotton

TABLE II
Adsorption of Sulphonated Oil by the Fiber

No.	Gm. of cloth	Gm. of oil used	Gm. of oil adsorbed	C	x/m
1a	2.0245	5.0	0.0931	4.9069	0.0459
1b	2.1111	5.0	0.1090	4.8910	0.0517
2a	2.0801	10.0	0.2619	9.7381	0.1259
2b	2.1416	10.0	0.3584	9.6416	0.1673
3a	2.0800	15.0	0.3640	14.6360	0.1750
3b	2.0950	15.0	0.4315	14.5685	0.2060
4a	2.0600	25.0	0.5581	24.4419	0.2709
4b	2.0675	25.0	0.6254	24.3746	0.3024
5a	2.0901	37.5	0.8499	36.6501	0.4067
5b	1.7508	37.5	0.7481	36.7519	0.4276
6a	2.0700	50.0	0.9668	49.0332	0.4671
6b	1.7410	50.0	0.8553	49.1447	0.4901

Average of a and b

No.	C	x/m
1	4.8990	0.0488
2	9.6899	0.1466
3	14.6023	0.1905
4	24.4083	0.2868
5	36.7010	0.4177
6	49.0890	0.4786

Colloidal Alumina with Turkey-red Oil or with Soap.—5 c.c. of Turkey-red oil were used in each experiment, but the concentration of aluminium acetate was varied. It was found that through a narrow range a precipitate formed which settled leaving a supernatant liquid which could be filtered. However this filtrate was slightly opalescent. On either side of the precipitating region a white homogeneous solution was formed which passed through filter paper unchanged.

According to Knecht[1] vegetable oils are used exclusively for the mordanting of cloth, olive oil being superior to all others. The oil must be rancid which means it contains more or less fatty acids (oleic acid and others). This oil forms a milky emulsion with sodium carbonate which is readily adsorbed by the fiber. In other words it is a soap solution containing emulsified oil, glycerin and other impurities. It seemed, then, that the soap is essential for fixing the alumina on the fiber.

A tenth-normal solution of sodium oleate was prepared from Kahlbaum's neutral dry sodium oleate, 25 c.c. of this soap solution were used for each experiment, the concentration of aluminum acetate was varied as in the case of Turkey-red oil. Again a narrow range was found where the precipitate settled leaving a slightly opalescent filtrate. On either side a homogeneous colloidal solution was formed which could not be filtered. A number of large extraction thimbles were coated with collodion and placed in tight-stoppered glass jars. The solutions of various concentrations of aluminium acetate and soap were placed in these collodion-coated tubes and allowed to filter for three weeks. At the end of that time about one half of the solution had filtered through perfectly clear, thus showing that in every case the colloid had been removed. Furthermore if a solution of colloidal aluminium soap be held at 85°C for a few hours it precipitates completely, or precipitates immediately at the boiling point.

Adsorption of the Dye by Alumina.—A suspension of alumina was prepared by precipitating Baker's aluminium chloride with ammonium hydroxide. The precipitate was washed twice by decantation and then filtered and washed on the filter paper. This wet precipitate was then washed into a bottle and shaken with distilled water to obtain uniform distribution of the particles. 50 c.c. were evaporated to dryness ignited and weighed. 0.8087 grams Al_2O_3 were found. 2.88 grams of alizarin were dissolved in the theoretical amount of sodium hydroxide to give sodium alizarate and the solution made up to one liter. 50 c.c. portions of the alumina suspension were pipetted into erlenmeyer flasks, varying amounts of dye were added to each and enough distilled water to make a total volume of 200 c.c. These were allowed to stand for twenty-four hours. The supernatant liquid was decanted onto an ashless filter and the amount of alizarin determined in an aliquot part. From this value the total alizarin in 200 c.c. was calculated. All the filtrates were neutral to litmus.

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[1] Knecht: "A Manual of Dyeing," **2**, 581 (1910).

Analysis of Alizarin.—Knecht's method[1] for the determination of alizarin by titration with titanous chloride was found to be unsatisfactory. The method adopted was based on the colorimetric estimation of colloidal alizarin in an acid solution. So long as the concentration of alizarin is not too great the finely divided alizarin remains in suspension for days. An excess of acid does not affect the results. The following procedure was found to be very satisfactory.

A standard dye solution was prepared by dissolving 0.36 grams of alizarin in sodium hydroxide and diluting to one liter. 20 c.c. of this stock solution was then diluted to one liter. One c.c. contained 0.0000072 grams of alizarin.

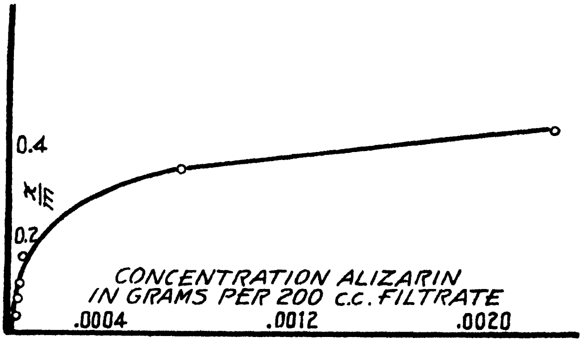

FIG. 2
Adsorption of Alizarin by Alumina

The standards were used in 100 c.c. Nessler tubes. Twelve standards were prepared by employing one c.c. of standard alizarin for number one and increasing the concentration of each succeeding tube by one c.c. After the addition of about 50 c.c. of water and 1 c.c. of sulphuric acid (1:2) the volume was made up to the mark. If the unknown solution for comparison was too concentrated, it was suitably diluted. By following this method it was possible to estimate the total amount of alizarin in 1 c.c. sample to 0.000000036 grams.

The data for the adsorption of the dye by hydrous alumina are shown in Table III and graphically in Fig. 2.

TABLE III
Adsorption of Dye by Hydrous Alumina

No.	Gm. dye used	Gm. dye in filtrate	x/m
1a,b.	0.0288	0.0000288	0.03558
2a,b.	0.0576	0.0000360	0.07119
3a,b.	0.0864	0.0000432	0.10680
4a,b.	0.1440	0.0000576	0.17810
5a,b.	0.2880	0.0007200	0.35523
6a,b.	0.4320	0.0023040	0.53142

[1] Knecht and Hibbert: Chem. Abs., **10**, 823 (1916).

Fig. 2 is a typical adsorption isotherm showing that alizarin is adsorbed by the hydrous alumina in the absence of calcium.

Stripping of the Dye by Sodium Chloride and Sodium Sulphate.—50 c.c. portions (0.7900 g Al_2O_3) of a suspension of hydrous alumina were pipetted into erlenmeyer flasks, 25 cc of sodium alizarate (1.2 g. alizarin per liter) were added and the flasks allowed to stand over night. The supernatant liquid appeared free from dye. Various amounts of salt solutions (2.4166 N) were added together with enough distilled water to make a total volume of 125 c.c. Two samples were made up without salt solutions as a check on the amount of alizarin adsorbed under the same conditions in the absence of added salt. The flasks were then allowed to stand for four days after which the solutions were filtered and analyzed for alizarin as described above. The data are summarized in Table IV and shown in graphic form in Fig. 3.

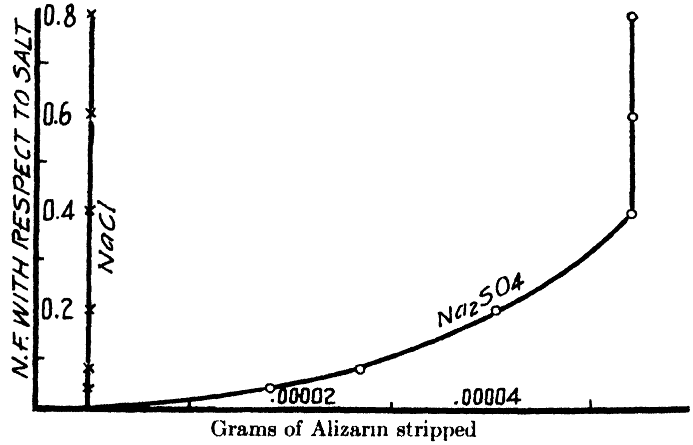

FIG. 3
Stripping of Dye by Salts

TABLE IV

Stripping of Dye by Sodium Chloride and Sulphate

No.	Salt	N.F. of Sol. with respect to salt	Gm. of alizarin in filtrate	stripped	% alizarin stripped
1a,b.	None	0.0	0.000027	—	—
2a,b.	NaCl	0.0403	0.000027	—	—
3a,b.	”	0.0806	0.000027	—	—
4a,b.	”	0.2014	0.000027	—	—
5a,b.	”	0.4028	0.000027	—	—
6a,b.	”	0.6043	0.000027	—	—
7a,b.	”	0.8055	0.000027	—	—
8a,b.	Na_2SO_4	0.0403	0.0000450	0.0000180	0.060
9a,b.	”	0.0806	0.0000540	0.0000270	0.090
10a,b.	”	0.2014	0.0000675	0.0000405	0.135
11a,b.	”	0.4028	0.0000810	0.0000540	0.180
12a,b.	”	0.6043	0.0000810	0.0000540	0.180
13a,b.	”	0.8055	0.0000810	0.0000540	0.180

Fig. 3 shows the stripping action of sodium chloride and sodium sulphate on the adsorption complex formed by alumina and sodium alizarate. No stripping action is noticeable with sodium chloride, presumably because the impure alumina was already saturated with chloride ion; the alumina was prepared from aluminium chloride; and no more could be taken up at that concentration of sodium chloride, to cause a noticeable displacement of the strongly adsorbed alizarin anion. But with sodium sulphate there is an adsorption of sulphate ion which causes a partial displacement of alizarin from the alumina. The percentage of alizarin displaced was very small.

Calcium Alizarate.—A solution of calcium acetate 0.01 N was prepared and treated with sodium alizarate (1.2 grams alizarin per liter) according to the following scheme: 50 c.c. of the calcium acetate were measured into 14 erlenmeyer flasks, varying amounts of dye were added, and the total volume made up to 150 c.c. The flasks were allowed to stand for 24 hours, after which the solutions were filtered and the amount of alizarin determined in the filtrate. The first eleven flasks contained a precipitate, while the last three were completely free of solid matter. The precipitate had dissolved in an excess of sodium alizarate. The results are tabulated in Table V, and plotted in Fig. 4.

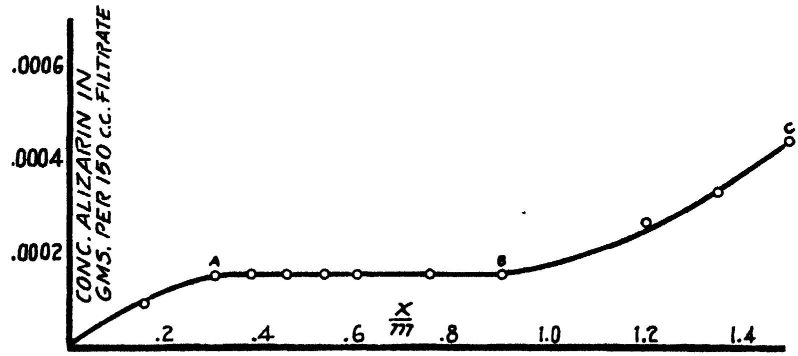

FIG. 4
Action of Sodium Alizarate on Calcium Acetate

Fig. 4 is a most interesting diagram. O to A represents the salting out effect of calcium acetate. That is, the relatively high concentration of calcium ion decreases the solubility of the alizarate. From A to B the calcium alizarate is formed without undue influence of the calcium acetate. At B peptization of the salt by sodium alizarate begins to appear and from C on there is complete peptization.

The solubility of calcium alizarate, as calculated from this diagram, is 0.00012 grams per 100 c.c. of solution at room temperature.

Adsorption of Soap by Alumina.—50 c.c. of a tenth normal soap solution were shaken with about ten grams of ignited alumina and filtered. The alumina was prepared by precipitating aluminium chloride with ammonium hydroxide. The filtrate was neutral to phenolphthalein and methyl orange, and when acidified with hydrochloric acid no precipitate was formed. The

TABLE V

Formation and Peptization of Calcium Alizarate

No.	Gm. dye used 150 c.c.	Gm. dye in 150 c.c. filtrate	Gm. dye taken up per 1 gm. $Ca(Ac)_2$ (x/m)
1a,b.	0.0060	0.00009	0.1496
2a,b.	0.0120	0.000151	0.3000
3a,b.	0.0150	0.000151	0.3760
4a,b.	0.0180	0.000151	0.4519
5a,b.	0.0210	0.000151	0.5279
6a,b.	0.0240	0.000151	0.6038
7a,b.	0.0300	0.000151	0.7557
8a,b.	0.0360	0.000151	0.9069
9a,b.	0.0480	0.000259	1.2084
10a,b.	0.0540	0.000324	1.3590
11a,b.	0.0600	0.000430	1.5081
12a,b.	0.0720	—	—
13a,b.	0.0840	—	—
14a,b.	0.0960	—	—

alumina had removed the soap from solution as the original soap solution was strongly alkaline to the indicator and gave a precipitate of fatty acid with the mineral acids.

Discussion and Interpretation of Results

Bancroft[1] objects to the use of alum or aluminium sulphate baths for mordants because the sulphate coagulates the hydrolyzed salt so readily that large amounts of alumina or basic salt are precipitated in the bath or in the fiber in such a form that it readily rubs off. He suggests the use of aluminium salts of organic acids, which hydrolyze more easily than the sulphates and yet keep the colloidal alumina peptized in a finer state of subdivision.

Napier[2] states that aluminium acetate has several advantages over the sulphate in that acetic acid is not so harmful to the dye; it has less affinity for the alumina, and consequently yields the alumina during the drying process of freshly mordanted fibers.

From the above it is evident that if alumina is adsorbed by cotton a greater adsorption will be shown with aluminium acetate solutions than any other. A glance at the data of Table I shows that cotton has a very feeble adsorbing power for alumina.

Since it is the alumina which has the lake-forming properties, some substance must be found which has a great affinity for the alumina and also for the fiber. Turkey-red oil has been found to be such a substance. It runs about 50% fatty acid, but the general character of the graph will not be changed whatever the fatty acid content may be. An examination of Fig. 1 shows that a smooth curve is obtained, free from sudden breaks, indicating the adsorption of Turkey-red oil by the cotton.

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[1] Bancroft: J. Phys. Chem., 26, 515 (1922).

[2] Napier: "A Manual of Dyeing," 121 (1875).

The experiments with Turkey-red oil and soap solutions show that whenever they come into contact with aluminium salts a colloid is formed. Therefore if sulphonated oil or any soluble soap be adsorbed by the fiber and this brought into a bath of aluminium acetate, a colloid is formed which is fixed to the fiber. And since experiment shows that alumina removes soap from solution, the above-mentioned colloid must be due to the adsorption of alumina from solution by the sulphonated oil or soap. In fact the fiber is mordanted with alumina fixed by the oil or soap. The same reasoning applies to mordants produced by sulphonated oils or soaps with iron, chromium, tin, etc.

Heat coagulates this colloid, which then has the property of adsorbing more sulphonated oil or soap, and this can adsorb more alumina. This is a property made use of by the dyers who repeat the oiling and metallic mordanting process several times in order to obtain a suitable amount of oxide on the fiber. The mordanted fiber is stoved before each new application of mordant.

Liechti and Suida[1] were of the opinion that alizarin is not taken up by alumina in the absence of calcium; but that in the presence of calcium a calcium aluminium alizarate lake is formed. Davison[2] found that hydrous alumina prepared from aluminium acetate, in the absence of calcium salts, takes up more alizarin than that prepared from the sulphate. When basic aluminium sulphate is used as mordant, the calcium eliminates the sulphate.

Williamson[3] investigated the aluminium lake of alizarin and came to the conclusion that the lakes are adsorption complexes of sodium alizarate and hydrous alumina, and that aluminium alizarate was not formed since the hydroxide equivalent to alizarate was not set free as would be the case if a double decomposition took place.

Weiser and Porter[4] object to the latter conclusion on the basis that whenever hydrous oxides are brought in contact with salts which yield a strongly adsorbed anion, it is the anion and not the molecule of salt which is adsorbed. They employed an alumina gel which was peptized by sodium alizarate and precipitated with an excess of the sodium alizarate. After this precipitate had settled, the supernatant liquid was nearly colorless, showing that the dye had been practically all removed. They analyzed this liquid and found almost as much sodium present as was originally combined with the alizarin.

Weiser and Porter report that the sodium was present in the clear supernatant liquid as sodium chloride. Therefore the chloride ion was originally present in the alumina gel as ammonium chloride. What Weiser and Porter proved was that adsorbed free alizarin is red. In acid solution one gets a red from the free alizarin which is apparently dissociated very completely. In alkaline solutions, one has sodium alizarate or calcium alizarate as the case may be. The fact that calcium alizarate is so insoluble means that a red containing lime will be faster to washing than a red which is either sodium alizarate or free alizarin.

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[1] Liechti and Suida: J. Soc. Chem. Ind., 5, 525 (1886).

[2] Davison: J. Phys. Chem., 17, 737 (1913).

[3] Williamson: J. Phys. Chem., 28, 891 (1924).

[4] Weiser and Porter: J. Phys. Chem., 31, 1824 (1927).

The goods after the dyeing operation possess a dull red color, which is transformed by the brightening process into the brilliant Turkey-red shade. The brightening of the color consists in washing out the excess oil and dirt collected from the various operations with soap. Some dyers recommend the addition of sodium carbonate. The addition of the latter is very detrimental, as the presence of the strongly adsorbed hydroxyl ions, formed by hydrolysis, tend to strip the dye from the fiber.

Kutschera and Utz[1] have shown that the high temperature produced when a piece of cloth mordanted with chromium and dyed with alizarin is steamed, makes the dye faster to washing. In order to account for the fastness to washing and the change in color one must postulate an increase of particle size. If the particles increase in size, their solubilities decrease. It has long been known that owing to difference in the variation of the absorption of light with varying thickness of the absorbing agent, a substance may be one color in films and another in thicker masses. Keane and Scheetz[2] have shown that yellow bricks are obtained by burning highly calcareous clay even though the iron content is higher than that which would give a red brick if the lime were not present. Bancroft[3] states that it is probable that the ferric oxide is present in such a fine state of subdivision that it is yellow and not red. This, then, is probably the case in Turkey-red dyeing. The particles of calcium alizarate are so finely divided that they appear dull yellowish red when the fabric is taken from the dye bath. The hot clearing bath or steam bath provides suitable conditions for the growing of larger particles at the expense of the smaller ones, just as the particles of barium sulphate grow larger on digestion. These larger particles appear bright red, and of course, are more insoluble than the smaller ones, thus increasing the brilliancy and the fastness to washing. It may be that there is some precipitation of an adsorption complex of lime and alizarin, just as there is with hydrous copper oxide and eosinic acid.[4] If so, the steaming would tend to convert it into calcium alizarate.

Mullin[5] discusses the brightening of colours by heat as follows: "Haller and Rupert report some interesting work upon the orientation of coloring matters within acetate silk and other fibers. When acetate silk is dyed at low temperatures with Para-Red, it has a yellowish shade, the dye being uniformly distributed within each fiber. After immersion in hot or boiling water, the shade becomes redder and the dye agglomerates into larger particles. Similar results are obtained, although with greater difficulty

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[1] Kutschera and Utz: J. Soc. Chem. Ind., **5**, 532 (1886).

[2] Keane: J. Phys. Chem., **20**, 734 (1916): Scheetz: **21**, 570 (1917).

[3] Bancroft: "Applied Colloid Chemistry" 242 (1926).

[4] Mullin: "Acetate Silk and its Dyes," 116 (1927).

[5] Gilbert: J. Phys. Chem., **18**, 586 (1914).

(steaming under pressure is necessary), when Para-Red is obtained from naphthol AS instead of β-naphthol, or when aminoazobenzene is used instead of p-nitroaniline.

"Similar changes are observed in nitro silk dyed with the same dyes and also with Indigo, Thioindigo Red, and Indanthrene Blue. Nitro silk dyed cold with Naphthylamine Claret (α naphthylamine coupled on the fiber with β-naphthol) contains the dye evenly distributed. When heated in water under one atmosphere pressure the dye agglomerates slightly without change of shade, but when heated for a prolonged period in boiling water or subjected to a short steaming under six atmospheres pressure, agglomeration becomes complete, the dye migrates towards the surface of each fiber and is deposited there as well-defined crystals which may be removed by washing and pressing, the fibers being thereby decolorized. Thioindigo Red dyed on nitro silk behaves similarly. Chrome Yellow, from lead acetate and a dichromate, dyed on nitro silk, is at first evenly distributed, but after steaming under four atmospheres pressure, agglomerates, and becomes orange, even in the absence of alkali, although no migration of the pigment occurs.

"Similar changes are observed by steaming dyed cotton, except that the agglomerated dyes migrate to the boundaries of the lumen in each fiber as well as to the cuticle, the migration, change of shade, and condensation or crystallization of the particles of dye being favored by prolongation of the steaming or rise of temperature. Vat dyes, Indigo, and Thioindigo Red easily, and Indanthrene Red 5GK, Indanthrene Brilliant Violet RK, and Indanthrene Blue RS with greater and increasing difficulty, crystallize and migrate within cotton fibres to the lumen and cuticle when steamed, accompanied by a change in shade. Uncertain results are obtained by steaming cotton dyed with direct dyes.

"Alizarin Red dyed on cotton mordanted with aluminium acetate is evenly distributed within each fibre, but when steamed for an hour under a half atmosphere pressure the pigment agglomerates and migrates to the lumen and cuticle. That deposited near the cuticle is removed by washing with water, the fibre being left colorless. Under similar conditions the presence of Turkey-red oil considerably retards the agglomeration and migration, and the dye which migrates to the cuticle cannot be removed by washing. The decrease in fastness to rubbing produced by steaming cotton dyed with indigo is due to migration of the dye to the cuticle of each fibre.

"Haller reports work of a similar nature upon the color changes of the blue and violet benzidine dyes on cotton, wool, and acetate silk, especially on touching the dyed cotton with a hot iron. His experiments are stated to confirm the view that these dyes form colloidal solutions of different degrees of dispersion, the larger particles coloring the cotton fibre blue, the smaller corinth-red. Solutions of a low degree of dispersion are particularly sensitive to temperature changes or to variations in the medium employed. Thus, in hot dye baths, wool and cotton are dyed red by aqueous solutions; but on cooling, the color on the bottom becomes blue-violet. Alcoholic solutions hardly affect wool but dye cotton a permanent corinth-red.

"The effect of touching the dyed cotton with heated metal is to increase the degree of dispersion of the dye in the fabric, with a change of color from blue to red. The addition of hydrazine hydrate to aqueous Diamine Blue 3R solution causes a similar change, and the solution will then dye cotton corinth-red. The absorption of the dyes by fibrous alumina and barium sulfate indicates a fixed relationship between the degree of dispersion of the dyestuff and that of the absorbent. The surface of the absorbent plays a decisive part also when fibres are used, for swelling causes inner micellar surfaces to come into play, the difference in the sizes of these accounting for the different behavior of different absorbents.

"Wool and acetate silk, after swelling, have larger inner surfaces than cotton. Thus an alcoholic solution of Diamine Blue 3R causes swelling of acetate silk and dyes it corinth-red. After saponification with sodium hydroxide, washing the fiber, and acidifying, the color changes to blue, showing that during saponification the inner structural conditions are changed. The reddening of blue-dyed cotton is also produced by desiccation over sulfuric acid, but to a less extent than by heating. The observed color changes on heating, and drying may thus be connected with dehydration and simultaneous increase in the degree of disperison of the dyestuff within the fiber."

The addition of tin crystals to the dye bath or the clearing bath cannot correct for the iron present, because ferrous and ferric iron both give a violet color with alizarin on an alumina mordant. If a tin-alumina-alizarin complex was formed, the final product would be more yellow in color since alizarin dyed on an alumina mordant in the presence of tin salts is yellow to orange. Consequently the only purpose of the tin salt in the clearing bath is to form a tin soap colloid which is adsorbed on the color lake. This acts as a varnish which cuts down the scattering of light from the surface of the pigment, and at the same time forms a protective coating.

A Short Process for Turkey-Red Dyeing

It has been shown that in Turkey-red dyeing as practised today there are really four things to consider; namely, the relation of the fixing agent to the fiber, the relation of the metallic mordant to the fixing agent, the relation of the dye to the metallic mordant, and the brightening operation. Furthermore one sees that the fixing of the metallic mordant on the fiber is the most clumsy, unscientific, and lengthy process of all. Therefore in order to shorten the actual time required for dyeing this color, the greatest opportunity for improvement is offered in the application of the latter.

Since alumina adsorbs soap from soap solutions, and soap adsorbs alumina from aluminium salt solutions, the problem resolves itself into the preparation of a colloidal solution of alumina and soap, then fixing such a colloid on the fiber; provided it is adsorbed by the fiber.

Experimental

Preparation of the Mordant.—A colloidal solution was prepared from N/10 sodium oleate and 0.2N aluminium acetate solutions. Sodium oleate was selected because of its great solubility; and aluminium acetate because the salts of the weakly dissociated organic acids do not have the coagulating properties possessed by the salts of stronger acids. Consequently colloidal solutions of a greater alumina content can be prepared. Aluminium acetate of much greater concentration than 0.2N show considerable coagulating effects and greater care must be exercised in the preparation of the mordant.

A series of mordant baths was prepared, each bath containing 25 c.c. of the soap solution, but increasing amounts of aluminium acetate from 5 c.c. to 200 c.c. Strips of wet standard cotton were dipped into each and then well washed in cold distilled water. The strips were cut into two pieces. The colloid was fixed on one piece by heating in boiling water; on the other piece by stoveing at 50 C for 18 hours. The samples were then all placed into one dye bath of alizarin and dyed in the usual manner. The samples which were heated in boiling water for a few minutes appeared to take the dye as well if not better than those which had been stoved. Concentrations above 25 c.c. of aluminium acetate take the dye best. The mordant composed of 25 c.c. soap solution and 100 c.c. of aluminium acetate was chosen for all the following experiments. Boiling water was used as the fixing agent.

Amount of Colloid fixed on the Fiber.—Strips of wet cotton were dried in a drying oven at 105° for two hours. The strips were then placed in glass-stoppered weighing bottles, allowed to cool and weighed. The strips of cloth were thoroughly wetted in boiling distilled water and placed in cold water before the mordant was applied. They were immersed in the mordant bath for 15 seconds. The cloth was next washed in distilled water at room temperature, and then placed in boiling water for 30 seconds. This process was repeated, with sample number two, three times; and nine times with sample number three. After the mordant had been applied the samples were dried at 105 C and weighed. The data of Table VI shows that the grams of mordant fixed per gram of cotton is practically a linear function of the number of times the mordanting process was repeated. Sample number three was ignited and the residue dissolved in nitric acid. A heavy precipitate of aluminium hydroxide was thrown out with ammonium hydroxide.

TABLE VI

Amount of Colloid fixed on the Fiber

Gm. Cotton	Times mordanted	Gm. mordant per gram cotton
1.3549	1	.0021
1.3907	3	.0045
1.3389	9	.0152

Adsorption of the Mordant by Cotton.—500 c.c. of the mordant was prepared from 400 c.c. of .2N aluminium acetate and 100 c.c. of N/10 sodium oleate solutions. Varying proportions of this stock solution were measured into erlenmeyer flasks and sufficient water added to make a total volume of 150 c.c. The total solids are equal to the number of grams of dry normal aluminium acetate and sodium oleate. Thus the total solids in 1 c.c. of stock solution are equal to 0.017 grams.

Strips of cotton were dried and weighed as described above. They were then thoroughly wetted with water, and placed in the flasks containing the mordant of varying concentrations. After standing for 24 hours the cloth was well washed in distilled water, dried and weighed. The gain in weight represents the amount adsorbed. The experimental data are given in Table VII and shown in graphic form in Fig. 5.

Examination of Fig. 5 shows that the mordant is adsorbed by the cotton fiber.

Dyeing.—Pure alizarin on an aluminium mordant in the presence of calcium salts produces a dark pink color and not the fiery Turkey-red. Accord-

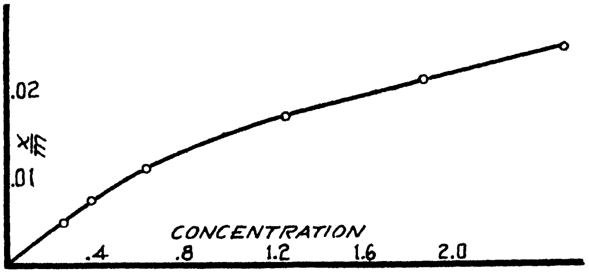

FIG. 5
Adsorption of Alumina Soap Colloid by Cotton

TABLE VII
Adsorption of the Mordant by Cotton

No.	Gm. Cloth	Total solids used	Gm. mordant adsorbed	C	x/m
1a.	1.2939	0.2550	0.0060	0.2490	0.0046
1b.	1.3622	0.2550	0.0067	0.2483	0.0049
2a.	1.3205	0.3825	0.0099	0.3726	0.0075
2b.	1.3526	0.3825	0.0091	0.3734	0.0067
3a.	1.2327	0.6375	0.0132	0.6243	0.0107
3b.	1.3098	0.6375	0.0144	0.6231	0.0110
4a.	1.2978	1.2750	0.0221	1.2529	0.0170
4b.	1.3034	1.2750	0.0223	1.2527	0.0171
5a.	1.3427	1.9125	0.0289	1.8836	0.0215
5b.	1.2663	1.9125	0.0267	1.8858	0.0211
6a.	1.2077	2.5500	0.0299	2.5201	0.0248
6b.	1.2695	2.5500	0.0323	2.5177	0.0253

Average

No.	C	x/m
1.	0.2486	0.0048
2.	0.3730	0.0071
3.	0.6237	0.0109
4.	1.2528	0.0171
5.	1.8847	0.0213
6.	2.5189	0.0251

ing to Knecht[1] alizarin "G", which is mainly a mixture of Iso- and Flavopurpurin containing some alizarin, is used for the dyeing of reds. A sample of alizarin "G" was kindly supplied by the "General Dyestuff Corporation" of New York City to whom I wish to express my appreciation. Standard cotton cloth was mordanted five times as described under the heading of "Amount of Colloid fixed on the Fiber". Without drying, the mordanted cloth was placed in a flask prepared with from eight to ten per cent of alizarin paste, containing twenty percent of alizarin. To this was added one to one and a half percent of solid calcium acetate. The cloth was treated in the dye-bath for about a quarter hour at ordinary temperature. After this the bath was gradually heated so that in about three quarters of an hour it began to boil and the boiling was continued for one and a half hours. The cloth was removed from the dye-bath and washed. It had a dull red color.

Brightening.—The cloth was placed in a large beaker filled with distilled water and kept at the boiling point for twelve hours. The color had changed to a deep red but was more or less without the brilliancy of Turkey-red. The cloth was next mordanted three times and boiled for three hours. After drying the color was a beautiful bright fiery red.

Fastness of the Color.—The fastness to light was tested by covering part of the sample with a thick card board, placing the entire specimen under glass and exposing it to the action of light from a northwest window of the laboratory. The exposed and unexposed parts were compared at the end of four weeks. The color apparently had not faded in the least.

Fastness to acids was tested by steeping a strip of the dyed material for one hour in a 5% solution of acetic acid. Another sample was boiled for 15 minutes in a solution containing 0.5 grams of sulphuric acid per liter. After the samples had dried they were compared with a piece of the original. The color remained practically unchanged.

Fastness to bleeding was tested by boiling a sample in distilled water for ten minutes. The water was allowed to cool and placed in a 100 c.c. Nessler tube and compared with distilled water. There was no noticeable difference in color between the two.

Discussion and Interpretation of Results

The data of Tables VI and VII show very clearly that cotton adsorbs the soap-alumina colloid which is easily and quickly fixed on the fiber by boiling water. By repeating the mordanting process any amount of mordant desired can be fixed on the fiber and in a very short time.

Soap is not essential in transforming the dull red produced in the dye-bath to the fiery red shade. However the brilliancy of the color is not brought out until the pigment is mordanted with some substance which has a higher index of refraction than air, which prevents the scattering of light at the pigment surface.

The experiments conducted in reference to fastness show that the color produced on the soap alumina mordant with alizarin "G" is exceedingly fast.

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[1] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 578 (1910).

Conclusions

In the old process for Turkey-red dyeing the cloth was freed from the resinous substances by treatment with sodium carbonate, and then allowed to bleach in the sun. This treatment removed the greater amount of lignin from the fiber yielding a more or less pure white cellulose which easily took up the "green liquor".

The second operation consisted in saturating the cloth in a bath ("first green liquor") containing an emulsion prepared by mixing sodium carbonate, rancid olive oil, and sheep or cow dung with water. Edward Bancroft[1] states that oil of sesamum, hog's lard, fish oil, or in fact any animal or vegetable oil may be employed. However he was of the opinion that the drying oils as linseed oil produce a blackening due to oxidation. After the goods are thoroughly saturated they are piled in heaps and exposed to the air until dry. They are then placed in stoves and heated at 60° for about 12 hours. This process is repeated three times.

The next four operations consist of treating the oiled yarn with solutions of sodium carbonate. A different carbonate bath is used for each treatment. By this process most of the surplus oil is removed from the fiber forming an emulsion which imparts a white color to the bath, hence the name "white baths". It is claimed that this treatment avoids the formation of so-called "surface" colors which rub off and smear.

After removal from the last "white liquor bath" the goods are well steeped in water at 55 C for 24 hours and stoved at 60°.

The materials used in the "green liquor baths" and "white baths" are soap-forming in nature. The method of treatment is conducive to the formation of soap. So in reality the bleached fiber now contains adsorbed soap and practically no free oil.

The tenth operation is known as "sumaching or galling". The cloth while still warm is steeped for six hours in a solution of sumach at 50° and then hydro-extracted. The cloth has now in addition to the soap taken up a certain amount of tannic acid. This latter operation, many dyers claim, may be omitted without affecting the color.

The cloth is now ready for the alum mordant. Alum is dissolved in water and a solution of about one fourth its weight of soda crystals are added, together with 15 to 20 percent of aluminium acetate and 0.5 to 0.7 percent of stannous chloride. However it is claimed by experienced dyers that the aluminium acetate and tin crystals are not essential. The goods are placed in this solution at 40 to 50 C for twenty four hours, then thoroughly washed and hydro-extracted. After which they are ready for the dye-bath.

In brief, the goods which contain adsorbed soap and tannin are brought into a solution of alum in which the free acid of hydrolysis has been partially neutralized; the temperature is raised which is favorable to further hydrolysis, thus making it easier for the soap and tannin to adsorb alumina from the solution, without excessive coagulation. Coagulation would be detrimental to the formation of a smooth mordant which will not rub off. As has been pointed out before, aluminium acetate is preferable to the sulphate since it hydrolyzes easier and to a greater extent without coagulation. Also any stripping of the dye by sulphates is avoided.

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[1] Edward Bancroft: "Experimental Researches concerning the Philosophy of Permanent Colours," **2**, 199 (1814).

The dye-bath is made up with hard water free from iron; or water to which has been added either ground chalk or calcium acetate; and ground madder or a 20 percent paste of alizarin "G". The goods are placed in the dye-bath and the temperature gradually raised to boiling during one hour and maintained at this point for about the same length of time. The goods are of a dull red color which is brightened by the clearing operations.

Calcium alizarate is a very insoluble salt which tends to make the dye more fast. Unless madder is used it is necessary to use so-called alizarin "G", which is a mixture of the purpurins with some alizarin, rather than pure alizarin. The latter produces pinks and not the fiery reds.

The thirteenth and fourteenth operations are called the "first clearing" and "second clearing" respectively. The "first clearing" consists in boiling the yarn in a soap solution and sodium carbonate. The "second clearing" bath is composed of a dilute soap solution to which has been added about 0.15 percent (of the weight of cotton) of stannous chloride.

The function of the "first clearing" is two fold. First, to remove all surplus oil and any dirt which may have accumulated during the various operations. Second, long heating at the boiling point is favorable for the growing of larger particles of calcium alizarate from the smaller ones, thus changing the color from the dull red to the fiery red. Soap as has been shown before is not essential for converting the dull red colored particles to the more brilliant form.

The "second clearing" bath likewise is favorable for the production of larger particles of calcium alizarate. In addition the stannous chloride and soap form a tin soap which is very strongly adsorbed on the surface of the dye pigment, acting as a varnish which prevents the scattering of light at the pigment surface. This varnish also acts as a protective coating, protecting the dye from rubbing and the action of chemicals.

In brief the process of dyeing Turkey-red as practiced may be summarized as follows:

1. The fiber is bleached.
2. Some soap-forming oil is adsorbed on the fiber.
3. The oil is saponified on the fiber.
4. The excess soap and oil is removed from the fiber.
5. The soap containing fiber adsorbs alumina.
6. The alumina adsorbs calcium alizarate.
7. The clearing operations remove the dirt, increase the size of the calcium alizarate particles, and varnish the dyed fiber with a very thin film of tin soap.

In the short process for dyeing Turkey-red, as proposed in this paper, an alumina-soap colloid is prepared from aluminium acetate and sodium oleate. The wet yarn when immersed in this mordant adsorbs the alumina soap colloid which is readily fixed on the fiber by boiling water. By repeating this process any amount of alumina can be fixed on the fiber.

The goods at this point are ready for the dye-bath without any further treatment; and possess an alumina mordant just as in the old process. As compared to the old method of dyeing this color, one has accomplished as much in one operation as with eleven of the original. Thus a great amount of time, labor and material is saved, as well as storage room, vats, heating stoves, fuel and so on.

The yarn is dyed as in the old process. The bath is composed of a mixture of 20 percent alizarin "G" paste, calcium acetate and water free of other metallic salts. The goods are immersed in the dye-bath and gradually brought to a boil and held at this point from an hour to an hour and a half. The yarn possesses a dull red or yellowish red color when it comes from the dye bath.

No strong clearing solution is needed for brightening this color, as there is no excess of oil to remove, and practically no way for the yarn to accumulate dirt during the two operations. Consequently the goods are steamed or boiled with water until the particles of calcium alizarate have increased to such a size as to produce a brighter red color. The yarn is again mordanted in the original mordant bath or in one prepared from stannous acetate and soap and again heated. The fibers are thus quickly varnished with an aluminium soap or tin soap which brings out the brilliant color desired.

The color as produced by the short process is probably just as bright, fast to light, washing, and so on, as any produced by the old time method.

Summary

1. Sulphonated oils are adsorbed by cotton.

2. Alumina is adsorbed feebly by cotton.

3. Turkey-red oil and soap solutions form colloidal solutions.

4. Alumina adsorbs soap from solution and soap adsorbs alumina from aluminium salt solutions.

5. Alizarin anion is adsorbed by alumina in the absence of calcium.

6. Sodium sulphate tends to strip alizarin anion from alumina.

7. Calcium acetate and sodium alizarate form a very insoluble chemical compound, calcium alizarate, which is peptized by an excess of sodium alizarate.

8. The function of the calcium ion when aluminium sulphate is used is to keep the sulphate from preventing the adsorption of alizarin by the alumina. Owing to its insolubility calcium alizarate gives a faster red than sodium alizarate.

9. Heating with steam or hot water after the dyeing operation is believed by Mullin to increase the size of the calcium alizarate particles in the lake,

thus changing the color from a dull yellowish red to the fiery red and increasing the fastness to washing. If there were any lime and alizarine adsorbed separately, the steaming would convert them into calcium alizarate.

10. The function of tin crystals in Turkey-red dyeing is to form a varnish about the pigment thereby increasing the brilliancy and fastness of the dye.

11. No calcium aluminium alizarate is formed.

12. A method has been proposed for the determination of small amounts of alizarin.

13. Cotton adsorbs a soap-alumina colloid.

14. The soap-alumina colloid is fixed on the fiber by boiling water.

15. Weiser's experiments indicate that small amounts of free alizarin adsorbed on an alumina mordant are completely dissociated giving the color of the alizarin anion.

16. Alizarin "G" produces the fiery reds.

17. The color can be brightened by boiling in water free from soap, but does not possess the brilliancy of Turkey-red.

18. The brilliancy can be produced by mordanting the dyed fiber with an alumina soap mordant and heating.

19. A quick method of mordanting with alumina has been proposed which is probably applicable to other metals, such as chromium, iron, and tin.

Acknowledgment

It is with great pleasure that I take this opportunity to express my sincere appreciation to Professor Wilder D. Bancroft at whose suggestion this investigation was undertaken. I feel greatly indebted to him for his kindly interest, helpful criticism, valuable suggestions, and encouragement throughout the progress of the work, and for the invaluable help in the prepatarion of this thesis. And especially do I wish to express my appreciation to my dear wife Mabel B. Parks, whose assistance and encouragement were invaluable.

Cornell University.

THE CHEMISTRY OF DISINFECTION*

BY WILDER D. BANCROFT AND G. HOLMES RICHTER**

The development of the problem of disinfection and antisepsis has undergone the usual series of events that one finds in the evolution of many problems of biology and medicine. In the race to gain new knowledge of this subject the empirical data have become quite voluminous, while the theoretical interpretations are very meager. Few, if any, of the theories of disinfection attempt to cover all phases of the subject, and up to the present time, these attempts have not been in keeping with the development of other branches of knowledge that have a direct bearing on this problem.

After the discovery of Lister, that phenol is an antiseptic, countless numbers of organic compounds have been tested, by empirical methods, for this property and many good disinfectants and antiseptics have been discovered. Since the demands of the professional men have been satisfied by the provision of fairly good drugs and our patience has been taxed by the trial and error methods, the time is now ripe to turn our thoughts to the theory of the action of toxic agents.

At the outset we realize that bacteriology is a descriptive science and can offer no basis for a theoretical interpretation. In dealing with the effect of drugs on living tissue we must realize the colloid nature of all living material and express our results in terms of colloid chemistry rather than clinical symptoms. The most outstanding and universal physical property of protoplasm is its colloidal structure. Theoretically it is possible to alter colloidal systems by chemical or physical means, the result being: coagulation or alteration of surface conditions such as swelling or contraction, displacement of adsorbed material, formation of emulsions, the increasing or decreasing of the charge on the particles, or reversal of the sign of the charge, peptization, formation of a jelly, stabilizing the sol, etc. The normal state of the colloids of any tissue varies with the age and the individual. Some of the variations, mentioned above, of the cellular colloids will bring about rather startling reactions in the tissue. For example it was found that a reversible coagulation was responsible for the action of anesthetics or narcotics.[1] Substances with a narcotic action when placed in contact with living protoplasm either directly or indirectly caused the colloids to coagulate. Upon the removal of the narcotic the colloids again became peptized to the normal state. In many cases these changes are easily observed with the aid of the ultra-microscope.

The case is just this, a direct narcotic enters the cell and is adsorbed upon the colloids to which it is most attracted. The first effect is the displacement

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** National Research Fellow in Chemistry.

[1] Bancroft and Richter: J. Phys. Chem., 35, 215 (1930).

of material that was already adsorbed upon the surface. The displacement of this normal material increases its "effective concentration" in the water phase. This increase in concentration, in accordance with the mass law, will speed up the chemical reactions which the substance is undergoing. This is nothing more than the stimulating effects on the chemical reactions of a cell by narcotics and toxic agents that have been observed by all workers. The greatest stimulating effect will be on those reactions that show a small tendency to be reversible, such as oxidations.

The accumulation of the narcotic upon the colloids of the cell eventually reaches such a point that the combined effect of the narcotic and the electrolytes of the cell will result in the coagulation. The slowing down of the diffusion of the material in the cell from the high viscosity of the coagulated protoplasm, and the blocking of the surface of the enzymes by the narcotic will result in narcosis.

An indirect narcotic does practically the same thing but in a different manner. Here the coagulating action is due to the products that accumulate through the interference by the narcotic of some normal function. Thus a substance that interferes with the adsorption of oxygen by the respiratory enzymes can behave as an indirect narcotic; the incompletely oxidized products such as acids will cause the coagulation.

Upon removal of the agent that is responsible for the coagulation, the colloids may be peptized again. If this happens there is a return to normal without any symptoms of toxic action. However if the surfaces of the colloid micellae have become so drastically altered that peptization does not take place upon removal of the agents that caused the coagulation, or if the agent is irreversibly adsorbed, then clearly, this effect can cause considerable damage to the affected tissue or cell.

Now a moment's reflection will show that always two effects, narcosis and toxic action, and nearly always a third, stimulation, can be obtained from one and the same substance. It is probable that the initial stimulation is always present, but if the increase in the effective concentration by displacement is negligible the stimulation may be overlooked. These effects are controlled by the concentration of the drug or more properly by the degree of adsorption. There is nothing astounding in this conclusion, it has been known from empirical data for a long time. Some prefer to regard it as a law and have named it the "Schulz-Arndt law". The only new thing about it is the correct explanation.

The organisms that are most frequently exposed, or are involved in man's attempt to expose them, to toxic agents are tho pathogenic bacteria and protozoa. The three stages or effect mentioned above are frequently observed.[1] Very low concentrations sometimes stimulate the organisms which we wish to kill, by increasing the concentration of the drug we can inhibit the growth, but not produce death until still higher concentrations are used. The inhibition of the organism by the drug is due to narcosis and the toxic effect of high concentrations is undoubtedly due to an irreversible coagulation. A closer analysis of this last phase of drug action is the object of this paper.

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[1] Archiv Hyg., 91, 231 (1922).

The first important question is whether the effects of drugs on an organism are physical or chemical. Colloid chemists for a number of years have been submitting evidence that dyes, electrolytes, drugs, and most organic compounds are only adsorbed upon bio-colloids. The work of Traube has been of great value because he has clearly emphasized the role of adsorption in drug action.[1]

Bechhold[2] also has presented a vast amount of data supporting this view. The quantitative experiments of Herzog und Betzel[3] show clearly that in the average case we are dealing with an adsorption of the drug upon the colloids of the organism. An application of the phase rule to such a system as organism-disinfectant showed that there was no definite chemical compound formed with a number of the common disinfectants. Thus the amount of disinfectant taken up by the organism is proportional to the concentration if the temperature is constant; and there is no possibility of a chemical reaction because there is no stoichiometrical relation between the two substances. The disinfectants that behaved in this manner were: silver nitrate, mercuric chloride, chloroform, and phenol. The only compound that showed evidence of a chemical reaction was formaldehyde, that is, the amount taken up was independent of the concentration of the formaldehyde. One can readily understand why it is active over a wide range of dilutions whereas other substances like phenol become inactive on dilution.

Perhaps the easiest approach to the problem is by first examining the effect of toxic electrolytes on lower forms of life. Wolfgang Ostwald[4] in his study of the toxic effect of electrolytes on living tissue recognized clearly that adsorption of the ion or molecule was necessary before any effect was produced and furthermore that the toxic effect was proportional to the adsorption.

What happens after the adsorption of the toxic ion takes place? Either one of two things can take place, there will be a tendency to increase or decrease the degree of dispersion, that is, peptize or coagulate the colloids of the cell. The colloid theory of narcosis has already indicated that irreversible coagulation is the most probable.

Most workers prefer to regard disinfection as occurring in at least two stages, the first being the true adsorption of the agent by the bacteria and the second step being the further action of the agent on the protoplasm. The first condition, that adsorption occurs, is generally accepted; the nature of the action after adsorption is subject to great differences in opinion, in spite of the logical conclusion that it is either a peptization or coagulation. There is a natural reluctance on the part of some workers to believe that dilute solutions of disinfectants can coagulate the cell colloids. Nevertheless, the work of Heilbrunn gives undisputed evidence that this is the case.

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[1] Biochem. Z., **19**, 197 (1919); **120**, 90 (1921).

[2] "Die Kolloide in Biologie und Medizin" (1929).

[3] Z. physiol. Chem., **67**, 309 (1910); **74**, 221 (1911).

[4] Archiv. ges. Physiol., **120**, 19 (1908).

Heilbrunn[1] in his study of the effect of mercuric chloride on the colloids of protoplasm gives us a clear picture of this coagulative effect. He says: "By actual viscosity tests it can be readily shown that low concentrations of mercuric chloride produce a coagulation, or at least a great increase in viscosity, in various types of protoplasm. *Arbacia* eggs treated with m/10000 $HgCl_2$ in sea-water very soon become altered so that the granules of the cell can no longer be moved by the centrifugal force. The same experiment can also be performed on protozoan cells. When the flagellate *Euglena* is centrifuged, it loses its spindle-shaped contour and becomes spherical, the granular inclusions massing at one end. But when a small quantity of mercuric chloride solution is added to the culture medium in which the *Euglena* lives, no shifting of the granules occurs when the protozoa are centrifuged. The protoplasm ceases to behave as a fluid and is a gel or coagulum. The coagulative action of mercuric chloride, at any rate in higher concentrations, apparently involves a precipitation of proteins from the hyaline ground-substance, that is to say the intergranular material, of the protoplasm. Not only is this a logical assumption, but there is also actual experimental evidence in its favor. When *Arbacia* are first centrifuged, and then treated with dilute solutions of mercuric chloride in sea-water, new granules can be seen to appear in the hyaline region previously free from granules.

"Dilute solutions of copper chloride which have little or no acidity may have a very pronounced action on protoplasm. Thus in one series of unpublished experiments, the following five solutions of copper chloride were prepared: m/1000, m/5000, m/10000, m/50000, and m/100,000. Even the m/5,000 was dilute enough so that there was practically no effect of the hydrogen ion concentration (the pH of this solution was 7.8). All the solutions produced a coagulative effect on sea-urchin eggs, as was clearly shown by centrifuge tests. This coagulation did not occur very rapidly. Thus a test of the eggs in the m/5000 solution showed no coagulation and no increase in viscosity after a 20 minute exposure, whereas a test after 54 minutes did show coagulation."

In these experiments the solutions are so dilute that there can be no question of an osmotic effect on the organisms, furthermore the pH of the solutions was normal so the effect can only be ascribed to the colloidal changes, that is, coagulation. Research workers in Naegeli's time were so completely mystified by this simple coagulation that they immediately named it "oligodynamic action".

Naturally, it is desirable to extend and confirm this work by using other disinfectants and testing for coagulation by a different method. Some experiments along this line have been carried out in this laboratory.

A direct observation of some of the colloids in the living cell of an organism is possible by using an ultra-microscope. If we work within the natural limitations of this instrument, then it is possible to satisfy our curiosity concerning coagulation by disinfectants and antiseptics. The yeast cell is an excellent object to start with and it is not too difficult to observe colloidal material within the cell. In addition, the work of Herzog and Betzel has already shown that yeast cells adsorb the disinfectants and that there was no chemical reaction except with formaldehyde. Thus these organisms are an ideal starting point.

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[1] "The Colloid Chemistry of Protoplasm" (1928).

Ordinary baker's yeast inoculated in Laurent's medium with 1.5% glucose was the stock culture. When fresh material from this culture was examined under the ultra-microscope one could see faintly some colloid material in Brownian movement. A photograph of the appearance of the normal cell is given in Fig. 1, the cells appear optically empty due to the fact that the light from the micellae is too faint to make an impression on the plate.

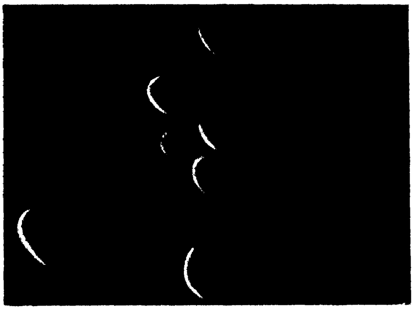

FIG. 1
Normal yeast cells

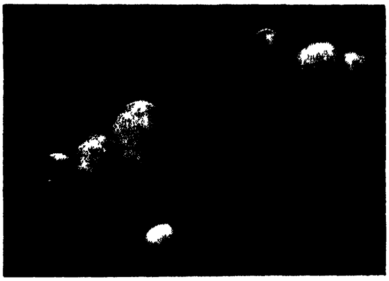

FIG. 2
Coagulated yeast cells

The culture was then treated with a solution of mercuric chloride until the concentration was about 1-1000. The material was then allowed to act for a short time and then again examined under the ultra-microscope. The bichloride has produced a drastic change in the colloidal make-up of the cell, the material is completely coagulated. Fig. 2 shows the appearance of the cells in the ultra-microscope. One can readily understand why the organisms die.

As mentioned above the effect can be either of two kinds, a reversible coagulation or an irreversible coagulation. If a substance merely produces a reversible coagulation, then it could easily inhibit the growth and give all external appearances of behaving as an antiseptic, because if removed, the organisms will again develop and show no ill effects. Chloroform is an example, it is a much better antiseptic than a disinfectant. De la Croix[1] showed that, generally, concentrations of 1-100 would inhibit the growth of bacteria but did not kill them until much greater concentrations were used. Koch[2] showed that this inhibition did not kill certain bacteria even if it were maintained over long periods of time. Ballner's[3] study of this phenomenon led him to the view that it was closely related to narcosis.

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[1] Archiv. exp. Path. Pharmakol., **13**, 175 (1881).
[2] Mitt. Kaiserl. Gesundsheitamt, **1**, 234 (1881).
[3] Z. Bakt., (2) **19**, 572 (1907).

This effect, a narcosis or aseptic state can also be demonstrated. Fig. 3 is a reproduction of a photograph of the same culture treated with a small amount of chloroform. There is a striking difference between this and the effect of the mercuric chloride. It is quite easy to reverse this coagulation, by merely washing the organisms with fresh media. The relation between these two types of action is that of the reversibility of the coagulation. In most cases in which irreversible coagulation is the ultimate result there is a preliminary stage in which reversibility is possible. On the other hand, substances that generally produce a reversible coagulation also produce an irreversible coagulation if allowed to act in higher concentrations. Thus it is difficult to draw a sharp distinction between a disinfectant and an antiseptic. It is also for this same reason that there is no sharp boundary between drugs classed as narcotic and toxic. Some theories are so confused on this point that they paradoxically explain narcosis and toxic action on the same basis! Thus the distribution coefficients of narcotics and toxic agents show no characteristic difference, the same is true of their surface tensions. *The distinction is not a physical property of the drug, it is the colloidal property of the protoplasm which determines whether the effect is narcotic or toxic.* Hence we can readily understand why the studies of Meyer and Overton, and Traube can never lead to a definite conclusion concerning the nature of narcosis or toxic action.

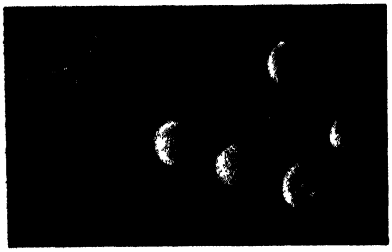
FIG. 3
Narcotized yeast cells

The effect of phenol on yeast was studied in the same manner. Herzog and Betzel have shown that there is no chemical reaction between phenol and yeast. The yeast only takes up the phenol in the sense of a physical adsorption. Dilute solutions of phenol are toxic to yeast, Herzog and Betzel state that .7% solutions will kill the cells after exposures of 5 hours. Phenol solutions of twice this concentration were prepared and diluted with an equal volume of the culture, the material was then examined under the ultramicroscope. As to be expected, coagulation occurred. The coagulation is quite marked after five hours. However, phenol and other agents, to be described later, did not show the same density of coagulation that $HgCl_2$ produces; thus there is a greater tendency towards antiseptic action than disinfection, at least in solutions of this concentration.

Since phenol is so generally used as an antiseptic it would be of interest to examine this effect on some other form of organism than yeast, *i.e.*, bacteria. It must be kept in mind that rather concentrated solutions are required to kill many bacteria. Thus in order to kill the following organisms in 15 minutes the concentrations of phenol required are:[1]

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[1] Biochem. J., 6, 362 (1912).

Pest and Typhus	7%
Diphtheria	5%
Coli	8%
Staphylococcus	10%

If weaker solutions are used a greater length of time is necessary before the organisms are killed; in still lower concentrations only inhibition is produced. The concentration of phenol in the two following experiments was 0.5%.

A pure strain of B. *Megatherium* was grown in the ordinary manner and a loop-full of the material was placed in 3cc of normal saline, an equal volume of 1% phenol was added; the concentration of phenol being 0.5 %. This material was then examined periodically in the ultra-microscope. At the end of two or three hours there was evidence of coagulation in a large number of the cells; another examination was made 48 hours later and the colloids of all the organisms were coagulated.

The same type of experiment was also tried on B. *Aerogenes.* In the same concentration of phenol as above there was no visible evidence of coagulation within the first two or three hours, at the end of 48 hours coagulation had taken place in all cells. In neither of the above experiments was the reversibility of the coagulation tested.

The observation of colloid material in these two bacterial cells is a little difficult, especially in B. *Aerogenes.* This is due to the smallness of the cells and also to their shape. The light reflected from B. *Aerogenes* when the substage mirror is at certain angles makes these organisms appear as coagulated diplococci. However, when all adjustments are carefully made there is no doubt that the effect of the phenol on these organisms is no different from that on yeast cells.

There are several different types of disinfectants and antiseptics: heavy metals such as mercury compounds, aliphatic compounds such as chloroform and carbon tetrachloride, aromatic phenols, oxidizing agents, and acid or basic dyes, or analogous substances. The evidence up to this point, based on the study of a representative member of the first three groups, shows that they all act in the same manner, *i.e.*, by coagulation. It is desirable to see if members of the other groups behave in this same manner. As a representative of the oxidizing class of compounds hydrogen peroxide was chosen, as it is a mild agent and no one would be inclined to believe that it was a coagulating agent. The experiment was performed on the same type of yeast culture as was used above. By means of a graduated pipette a given volume of the culture was treated with a three percent solution of hydrogen peroxide until a final concentration was 1%. This treated culture was permitted to stand for four hours and then examined in the ultra-microscope. The changes were quite marked, a very extensive coagulation had taken place.

The same type of experiment was next tried with Yatren,[1] an acidic substance. A solution whose concentration was 1-500 of the sodium salt of

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[1] The authors are indebted to E. H. Volweiler of the Abbott Laboratories for the samples of Yatren and Acriflavine.

Yatren was prepared and diluted with an equal volume of the yeast culture. The treated culture was allowed to stand for four hours and then examined as above. The culture used in this experiment was not pure, it was contaminated with some unidentified bacteria. The examination revealed that all the organisms were affected in the same manner, the colloids within the cells were flocculated.

The effect of Acriflavine on the organisms was next investigated. The culture in this case also was contaminated with foreign bacteria. The Acriflavine was made up to a concentration of 1-500 and diluted with an equal volume of the culture. After standing three or four hours the material was examined in the usual manner. In this case the yeast cells were slightly coagulated while the other organisms were not so affected, thus showing a selective action. The coagulation of the yeast cells is not marked as in the other cases and is reversible at this stage. Since the culture is acidic and Acriflavine is most active in alkaline media this effect was to be expected.

Thus from this superficial survey of the action of representative members of various groups of antiseptics and disinfectants, we are drawn to the conclusion that they all affect the organisms in the same manner, *i.e.*, by coagulating the colloids of the cell. This coagulation may be of two types, reversible or irreversible bringing about the conditions known as antisepsis or disinfection.

The kinetics of the coagulation of biological colloids offers an interesting study. The fact that the popular belief that there is a "relation between chemical constitution and physiological action" is evidence enough that many think that the effect of drugs on living tissues is, in the ultimate analysis, chemical. The justification of this view is based upon the fact that such phenomena can be expressed by the equations that are used to represent the velocity of chemical reactions. The literature is filled with studies showing that disinfection is a "monomolecular reaction".

This is indeed unfortunate; these equations that express velocities of chemical reactions are empirical and consequently are not specific for chemical reactions. They can express the velocities of physical processes with equal readiness, thus if we have a beaker full of a solution of a dye and turn a stream of water into the solution, the rate of disappearance of the dye follows the monomolecular equation. Or if a given volume is filled with a certain gas and another gas is blown in, the rate of change in the concentration of the gases can be represented by these equations. The rate of the dissolving of a crystal or the velocity of the swelling of gelatin in water can be expressed by the monomolecular equation, etc.

The velocity of coagulation of many sols, in certain regions, can also be expressed by these equations. Taking the data of Westgren and Reitstötter on the coagulation of a gold sol, we can express the data by the "bimolecular equation".

Time in min.	Rel. No. particles per cc	"K"
0	5.22	—
1	4.35	.0380
2	3.63	.0419
3	3.38	.0347
5	2.75	.0344
7	2.31	.0344

In spite of this good agreement, there can be no question of a chemical reaction, the process is purely physical. It is not surprising that many coagulations resemble chemical reactions, in the one case the velocity depends upon the collision of particles and in the other, collision of molecules. It is this same type of confusion that leads many to believe that the coagulation of proteins is a chemical process, or that disinfection is chemical in nature.

There is a characteristic difference however, between chemical and physical changes. This difference is in the acceleration of the velocity when the temperature is increased, for an increase of 10° the acceleration of the velocity of chemical changes is from 1.8 to 4, the average for a great number of cases is approximately 2.[1]

Cooper[2] has studied the effect of temperature on disinfection and has obtained some interesting results. The temperature range of his experiments was 17° (from 20° to 37°) and if purely chemical changes were taking place one should expect the effect of the disinfectant to be about four times greater at the higher temperature. Hydroxylamine hydrochloride, pyrogallol, m-cresol, and p-bromophenol acting on B. *Coli* were just as effective at the lower as at the higher temperature, the acceleration being zero. Phenol, hydrogen peroxide, ethyl alcohol, acetone, and quinol acting on B. *Coli* had a coefficient of 2-3 over this range. Picric acid, benzoquinone, toluquinone, quinhydrone, 2,6-dichloroquinone, and potassium permanganate acting on the same organisms had coefficients ranging from 10 to 20.

The coefficient of 2-3 for the phenol group indicates that a chemical reaction might be responsible for the effect. However, if the same series of disinfectants are tried on other organisms the above classification no longer holds, the individual members jump from one group to another depending upon the organism. One gathers the impression then that the effect of disinfectants, in the general case, is physical rather than chemical, this physical change being coagulation of the cell colloids.

There are other difficulties with a purely chemical concept of toxic action. In a typical chemical reaction one can predict accurately from a knowledge of the mass law the effect of varying the amounts of the reacting materials. Thus in the case of the reaction:

$$\text{alcohol} + \text{acid} \rightleftarrows \text{ester} + \text{water}$$

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[1] Taylor, "Treatise on Physical Chemistry".

[2] J. Hyg., **28**, 163 (1928).

an increase in the amount of the acid or alcohol will increase the velocity of the reaction toward the right side of the equation and increase the yield of ester and water. Or if either the ester or water is added, the reaction is displaced towards the left side of the equation with the corresponding increase in the amount of acid and alcohol.

Now assume a reaction between the bacteria and disinfectant:

$$\text{bacteria} + \text{disinfectant} \rightleftarrows \text{dead bacteria}$$

It is common knowledge that increasing the concentration of the disinfectant will increase the velocity of disinfection and the number of dead bacteria at the new equilibrium will be increased. An experiment of McClintic will illustrate this point.[1] With a constant amount of bacteria a dilution of disinfectant "B" 1-1600 had no effect on B. *Typhosus* in 15 minutes, a dilution of 1-1500 killed the entire culture in 10 minutes, a dilution of 1-1400 would do the same thing in 5 minutes, and a dilution of 1-1300 killed all the bacteria in 2½ minutes. This is in qualitative agreement with the mass action law.

The experiment can be carried out in yet another way. If dead bacteria be added to the disinfection experiment the effect of the disinfectant should be decreased, if the reaction is reversible. Lange[2] did this experiment and indeed the effect of the disinfectant was decreased. Up to this point there is an excellent qualitative agreement with the analogy of a chemical reaction. There is left only one other experiment to make the analogy complete, the investigation of the behavior of the reaction when the amount of *live* bacteria are varied. If larger amounts of live bacteria be used then on the analogy of a chemical reaction the velocity of disinfection should be much greater. Experiments with constant amounts of disinfectant and increasing amounts of bacteria reveal a hideous disagreement[3] with the idea of a chemical reaction. The increasing mass of the bacteria cut down the effect of the disinfectant to a marked degree. McClintic found that when the bacterial mass was increased five-fold the phenol coefficient of disinfectant "B" dropped from 15.6 to 11.6. In any experiment if the number of bacteria be made very great then there will be no effect produced by the disinfectant. The analogy therefore breaks down beyond repair and we are driven to the conclusion again that disinfection, as a general rule, does not depend upon chemical reactions for its basis.

Some workers prefer to abandon chemical concepts altogether and explain these results on a biological basis, with the aid of mathematics. This is not necessary, for the phenomena are colloidal and can be explained by colloid chemistry. It has already been shown that the biological effects are produced by coagulation. The coagulation in turn depends upon the adsorption of sufficient ions or particles of opposite charge to lower the stabilizing charge to the point of coagulation. The stabilizing charge of the cell colloids can also be lowered by the adsorption of organic non-electrolytes as Freundlich and Rona[1] have demonstrated and explained. In this case the coagulation is due to the combined effect of the organic compound and the electrolytes of the cell.

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[1] Hygenic Lab. Bull., No. 82 (1912).

[2] Z. Hyg. Infektionskrankh., 96, 108 (1922).

[3] Lange gives a summary of the literature up to 1922 in Z. Hyg. Infektionskrankh., 96, 117 (1922).

The colloids of the cell behave as the substrate upon which the disinfectant is adsorbed. The coagulation of these bio-colloids proceeds in the same manner as that of other colloids, there must be the adsorption of some minimal amount of the coagulating agent before flocculation begins. Increasing concentrations of the flocculating agent, within certain limits, will hasten the coagulation. Thus it is not surprising that increasing the concentration of disinfectant will hasten the process of disinfection. Suppose that dead cells are added to the experiment (cells killed by heat), these cells will also adsorb the disinfectant and lower its effective concentration and thus slow the process down. The addition of living cells does the same thing and they are not materially damaged if they are numerous enough because the amount of disinfectant per cell is less than that required to produce irreversible coagulation. The whole process is clearly colloidal in nature and depends upon adsorption and coagulation.

If this conclusion is correct then the methods employed in disinfection and antisepsis must all be methods of coagulating bio-colloids. The available data seem to indicate that this is indeed the case. One can further postulate that any method of producing narcosis in higher animals is likely to inhibit the growth and activity of the bacteria and if pushed far enough will behave as disinfectants.

Consider some of the less common methods of narcosis and see if the conditions outlined above are not fulfilled. A physical blow will cause narcosis. We are familiar with the effects of a sharp blow on the head or striking our "funny-bone". In the discussion of narcosis we have presented evidence that this is due to the mechanical coagulation of the cell colloids.[2] The effect of mechanical agitation on bacteria has been investigated by several workers and the data are very interesting. Two effects are at once apparent, at first there is increased growth and activity and later inhibition but not death.[3] The experiments are usually carried out by shaking bacterial suspensions in a shaking machine for several hours. The first effect on the cultures was to increase the growth activity above that of the unshaken controls. On shaking for longer periods of time it was found that the growth was greatly retarded, or completely inhibited. This is not due to any mechanical damage to the cells for the culture would grow in the normal way when removed from the shaker. Thus there is a true stimulation followed by narcosis, the effect being due to mechanical coagulation.

Heilbrunn[4] discusses many cases of coagulation of cell colloids by mechanical means and has measured the viscosity changes produced by the coagulation. The mechanical coagulation of other bio-colloids is by no means rare, the coagulation of blood fibrin, the inactivation of enzymes, and of immune serum by shaking are commonplace examples of this phenomenon.

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[1] Biochem. Z., **81**, 87 (1917).

[2] Bancroft and Richter: J. Phys. Chem., **35**, 215 (1931).

[3] Archiv. ges. Physiol., **17**, 125 (1878).

[4] "Colloid Chemistry of Protoplasm" (1928).

The practical importance of the antisepsis produced by shaking is nil, although from the theoretical point of view it is valuable because it shows clearly that the process of disinfection is colloidal in nature.

It has been known for quite a time that the injection of distilled water around a nerve will cause narcosis. The effect is explained by the coagulation produced. Let us see if this type of coagulation plays any role in disinfection. The effects of distilled water on bacteria are very interesting. Fisher[1] would have us believe that the deleterious action of distilled water on bacteria was due to "plasmopsis" of the cell *i.e.*, a bursting of the cell due to the high internal osmotic pressure. He was able to observe the degeneration of the exposed organisms. Leuch[2] carefully repeated these observations and found that the degenerated fragments could be seen even if the bacteria were originally absent; or if the glass slides were well cleaned there was no plasmolysis. One gathers the impression then that the osmotic effects are of only secondary importance and that the distilled water exerts its effect by some other means.

Concerning the colloidal mechanism of this action it is not unlikely that the bio-colloids of the cell are peptized by the electrolytes of the medium. There must be a minimum concentration below which the adsorption of the ions is not sufficient to peptize the material to the proper degree. When the addition of the distilled water has been sufficient to dilute the ions to this value the bio-colloids merely flocculate. The whole process is similar to the flocculation of sols that have been dialyzed too long, or the coagulation of globulins when they are diluted with distilled water. The flocculation, as in most cases, is more easily reversible in the earlier stages than at a later period. In keeping with this it is found that bacteria exposed to the action of distilled water for short periods of time are not damaged as much as when the exposure is longer. The practical importance of disinfection by this means is not worth mentioning. However, the theoretical value of this phenomenon must not be underestimated. It is a well-established phenomenon and is not dependent upon osmotic effects as Leuch has shown. Still no theory of disinfection except the colloid theory is able to account for the action on the same basis as other types of disinfection. There could be hardly a question concerning distribution coefficients, surface tension changes, or chemical reactions; yet there are prominent theories that rest upon these effects as a basis. This is just another example of the frequent deviation of fact from the theories that do not consider the colloidal nature of living matter.

The effect of heat on bio-colloids is well known and little persuasion is needed to convince one that it is coagulation. Disinfection by means of heat is quite common, the colloid aspects of this method are however, not often clearly recognized. Most workers agree that coagulation occurs. The disagreement arises in the different concepts of coagulation. Biological workers in general support the view that the process of coagulation by heat is chemical in nature. The principal basis of this view is that the velocity of coagulation can be expressed by an equation that is "characteristic" for the occurrence of a chemical reaction.[1] The mistake in this view lies in the assumption that the equation is specific for a chemical reaction. That such an assumption is wrong has already been illustrated in the case of the coagulation of a gold sol, which can also be fitted to the equation.

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[1] "Vorlesungen über Bakterien" (1903).

[2] Archiv. Hyg., 54, 396 (1905).

The temperature coefficients of heat disinfection are high and show no tendency to remain constant over equal ranges of temperature. This is exactly what one would suspect if the phenomenon were physical or colloidal and by no reasonable twist of the inagination could such evidence be used to support a chemical view. Bancroft and Rutzler[2] have investigated the effects of heat on protein bio-colloids and their conclusions are that the coagulation is colloidal throughout. Their paper should be consulted for the theory and many interesting details of the phenomena of heat coagulation.

Turning to a less well known method of coagulation, that produced by light, let us examine the role of light in disinfection. Concerning the coagulation of proteins by light of short wave-length, Mond[3] has clearly demonstrated that the colloidal condition of many bio-colloids can be altered. The investigations of Clark[4] support the theory that the action of ultraviolet light on organic substances consists in the emission of electrons from the material. In sols that had a negative charge, the loss of electrons by light action would leave neutral or positive particles, the mutual action of the positive and negative colloids would tend to coagulate the sol. On the other hand, a positive sol when exposed to ultraviolet light, loses electrons and becomes more positive, hence it peptized to a greater degree. Neutral sols become peptized through the positive charge gained by the loss of an electron. Clark was able to demonstrate these effects with egg albumin exposed to ultraviolet light.

The coagulation by light is also produced *in vivo*. Gibbs[5] exposed *Spirogyra* to the rays from a mercury vapor arc, and followed the colloidal changes by viscosity measurements. The variations of viscosity that are characteristic for coagulating protoplasm were found to take place. Addoms[6] was able to see the coagulation, by means of the ultramicroscope, in wheat seedlings root hairs exposed to ultraviolet light. Here, as in other types of coagulation, the process is easily reversible in the initial stages; the toxic effects are associated with the irreversible stage of coagulation.

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[1] T. B. Robertson: "Physical Chemistry of Proteins."

[2] J. Phys. Chem., **35**, 144 (1931).

[3] Archiv ges. Physiol., **196**, 540 (1922).

[4] Am. J. Physiol., **61**, 72 (1922).

[5] Trans. Roy. Soc. Canada, **20**, 419 (1926).

[6] Am. J. Botany, **14**, 147 (1927).

Light of short wave-length has the same effect on bacteria. As early as 1877 Downes and Blunt[1] discovered the bactericidal action of light. The most effective region of the spectrum is the range from 297 $m\mu$ to 210 $m\mu$, that is the same region that is most effective in coagulating proteins.[2] Furthermore the action is direct and does not involve the formation of bactericidal substances such as peroxides, etc., as the amount of these substances produced is far below that necessary to cause the large effects. Moreover, the action is evident only when the light is on; after the light is cut off there is very little action due to the effects of the small amount of peroxides formed during the illumination. We can conclude then, that the action is direct. When ultraviolet rays are passed through suspensions of bacteria only the rays that are adsorbed are effective in killing the organisms. As already mentioned, Henri showed that the region of the ultraviolet light possessing the strongest bactericidal power is that which is absorbed by bacterial proteins. Moreover, the degree of action is almost exactly proportional to the extinction coefficient of protoplasm for these rays. Hence, we can be drawn to only one reasonable conclusion, the toxic action of light is due to the coagulation of the protein colloids of the cell. This is in complete harmony with other types of disinfection and strengthens our belief that disinfection and irreversible coagulation, by whatever means, are intimately related.

Briefly recapitulating, we can observe by means of the ultramicroscope, that all types of chemical disinfectants bring about an irreversible coagulation of the bacterial colloids. Reversible coagulations of the colloids are associated with antisepsis. The corollary that coagulation, by whatever means, will result in antisepsis or disinfection is verified by the types of coagulation produced by distilled water, mechanical agitation, heat, and light. Furthermore, the coagulation is colloidal in nature and not chemical. The fact that disinfection data can be fitted to chemical reaction velocity equations is without significance. The colloid theory is the only theory that can adequately explain the types of disinfection produced by physical means. Thus, from every phase of disinfection we are drawn to the conclusion that the process is colloidal in nature and consists merely in the irreversible coagulation of the bio-colloids of the bacteria.

In the development of this thesis up to this point, it has been stated or otherwise assumed that the coagulation has been produced directly by the bactericidal agent. This is by no means necessary, for as we have already indicated there is a group of narcotics that act indirectly and the same possibility exists that such a thing may occur in disinfection. The experimental researches of C. Voegtlin have led him to conclude that the action of arsenic upon trypanosomes was indirect. In his own words: "A long series of experiments carried out in recent years at the U. S. Hygenic Laboratory in Washington has furnished evidence to the effect that arsenic enters into combination with a sulphur compound (glutathione) which is widely distributed in animal cells and even in such low forms of plants as yeast. This sulphur compound had recently been discovered by the English bio-chemist, Hopkins, who found it essential for the maintenance of normal cellular combustion. Now it is significant that certain sulphur compounds have a great affinity for arsenic, as every chemist knows. It was therefore very important to find that the toxic action of arsenic on the trypanosomes could be completely checked in the test tube as well as in the living animal by simply furnishing the cells with an extra supply of glutathione. The effect of the latter substance is quite specific, as it proved to be the only substance of a great number of others occurring in the body which offered protection. Without going into further details we may therefore assume that arsenic kills by interfering with the normal cellular combustion or oxidation mechanism, and the cells die of "internal asphyxia"."

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[1] Proc. Roy. Soc., **26**, 488 (1877).

[2] Compt. rend. soc. biol., **73**, 323.

We may question the conclusion that death is due to "internal asphyxia." This lowering of the oxidation process of the cell will allow the toxic (coagulative) substances that are normally destroyed by oxidation to accumulate to the point where they coagulate the cell colloids and cause narcosis or death, depending upon the reversibility of the coagulation. Hence, if the mechanism outlined above is true, arsenic behaves as an indirect disinfectant. Heffter has suggested, and supported by several experiments the theory that free sulphur acts upon the glutathione and forms complex sulfides which stop the cellular oxidation. This would explain the toxic action of sulphur. It may be that there are numerous examples of this indirect class in the reducing type of drugs, but actual knowledge is meager at present.

Since the death of the organisms is due to irreversible coagulation the question of reversibility and the conditions which favor it are important. Normally in testing disinfectants the organisms are exposed to the agent, then placed in some medium to observe whether growth takes place or not. Indeed, this is a convenient but not very accurate method, for the peptizing agents of different substrates are quite different. For example, Liesegang mentions a case where the bacteria of bird cholera were exposed to 1:1000 mercuric chloride solutions for seven minutes; these organisms were then unable to develop on ordinary media. One would ordinarily conclude that they were dead. However, this is not the case for if they are placed in their natural environment, birds, they begin to develop after three hours. The conditions favoring peptization are much better in the animal body than in the laboratory media. Süpfle[1] gives a striking example of peptization of *Anthrax* bio-colloids after treatment with mercuric chloride. The organisms after exposure are apparently dead when tested on ordinary media. Süpfle mixed these organisms with a good grade of blood charcoal and cooled the mixture, to aid the adsorption. In this case the sublimate is adsorbed much stronger on the charcoal than on the bacteria so the material leaves the *Anthrax* cells and is deposited on the charcoal. Upon removal of the charcoal, the organisms are found to be again normal and grow well on the ordinary media. In this way it was found that reversibility could be effected in organisms exposed to:

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[1] Archiv. Hyg., **89**, 351 (1920); **93**, 252 (1923).

5% sublimate	after	11	days
3% "	"	38	"
1% "	"	40	"

One can understand why it is much more difficult to disinfect living tissues with their favorable peptizing conditions, than inert substrates such as glassware, clothes, instruments, etc. The favorable peptizing conditions in the former case are probably the colloids of the tissue behaving like the charcoal in Süpfle's experiments. In the light of colloid chemistry the testing of disinfectants should be studied from the point of view of the reversibility of the coagulation produced by the disinfectant rather than the determination of growth, on relatively inert media, after exposure.

Some workers regard disinfection in a totally different light, thus McClendon[1] discusses disinfection under the head of cytolysis. However, he clearly recognizes that cytolysis does not always accompany death. Many anesthetics and disinfectants do actualy favor the cytolysis; from our knowledge of the effects of these drugs on protoplasm we can construct a mechanism of cytolysis. For example if a tissue is cut off from the blood supply it will after a time digest itself (autolysis); this is accelerated or favored by the presence of ether,[2] etc. We know that shortly after the oxygen supply is cut off narcosis occurs or a reversible coagulation of the tissue is produced; in time this passes into an irreversible coagulation and death. Autolysis occurs after this stage of irreversible coagulation and is brought about by the enzymes present in the tissue. It is known that the enzymes are not as easily affected as protoplasm by anesthetics or mild disinfectants. For example, when toluene is added to digestion experiments, it affects the protoplasm of bacteria and kills them while it is almost harmless to the enzyme. On the other hand, if the coagulation is extensive enough to damage the enzymes then autolysis cannot take place. Heilbrunn has studied the viscosity of protoplasm that is undergoing cytolysis and the evidence is that coagulation precedes digestion:

"In spite of the fact that Loeb many times emphasized the importance of the so-called cytolysis of sea-urchin eggs, he made little effort to explain the mechanism of the process. In pages 188 to 190 of his book he expresses some vague general ideas regarding the possible nature of cytolysis. Saponin and benzine, he states, dissolve the chorion or jelly of mollusc and annelid eggs. He then cites von Knaffl-Lenz's views to the effect that cytolysis is due primarily to the liquefaction of lipoids, and he makes the following quotation from von Knaffl-Lenz, "The mechanism of cytolysis consists in the liquefaction of the lipoids, and thereupon the lipoid-free protein swells or is dissolved by taking up water."

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[1] "Physical Chemistry of Vital Phenomena."

[2] Archiv. exp. Path. Pharmakol., 60, 256 (1909).

"Loeb thus apparently believes that cytolysis in sea-urchin eggs is primarily a liquefaction of the protoplasm. This it most certainly is not, for viscosity tests indicate beyond the question of a doubt that during cytolysis, the viscosity of the egg protoplasm increases enormously.

"Our general conclusion is that in all types of protoplasm there is a definite type of response to such agents as distilled water, fat solvents, the electric current, mechanical injury, etc. This response is typically characterized by the appearance of numerous small vacuoles within the protoplasm. Frequently, though not always, it is accompanied by an increase in the volume of the cell. When pigment is present in the cell, this always escapes."

The phenomena exhibited by the bacteriophage are also of this type although it is referred to as a lysis. To begin with it has been noted by several workers that small quantities of the bacteriophage stimulate the bacteria.[1] We have already indicated that in the coagulation of cellular bio-colloids the increasing instability of the system is associated with the phenomena of stimulation. This alone would indicate that displacement adsorption and coagulation are concerned in the action of the bacteriophage. The excellent researches of J. Bronfenbrenner present more direct evidence that the colloidal condition of the cell is changed before digestion and that the digestion is due to the normal endoferments. "When swollen bacteria are stained by the method of Gutstein, the cytoplasm may be differentiated from the ectoplasm. The latter always appears continuous, and even in extremely distended cells it shows no evidence of "holes" described by D'Herelle as resulting from the puncturing of the membrane by the entering parasites. The cytoplasm, on the contrary, shows marked changes during swelling. It takes the stain less intensely and less evenly as the swelling progresses, so that in many instances it appears segmented or beaded. In cells photographed at this stage unstained, by means of ultra-violet light illumination, the cytoplasm appears to be of uneven density, quite unlike that of normal bacteria."

"The lysis of bacteria in a synthetic medium, devoid of all protein, gave unmistakable evidence of hydrolysis of bacterial protein.

"In the light of these experiments, the clearing of bacterial cultures in the presence of bacteriophage seems to be due to the hydrolysis of the bacteria. The active agent (bacteriophage) plays no part in the actual solution. The solution is the result of intercellular digestion brought about by normal endoferments."

Bacteriologists do not know, at present, how these enzymes become activated. Colloid chemistry is able to suggest a mechanism; it is common knowledge that enzymes, as all catalysts, must adsorb or be adsorbed by the substrate before they can act. Colloidal studies have indicated that the adsorption capacity of coagulated proteins is frequently greater than that of the uncoagulated sol; this is probably due to the jelly structure of the coagulum. Consequently, we should expect that coagulated proteins should be more easily and rapidly digested; this has been found to be the case.[1] In regard to the swelling of the protoplasm referred to above, bacteriologists explain this as due to the increase in osmotic pressure within the cells.[2] Another possible explanation is that the swelling is due to the change in the pH of the cell during digestion, the degree of imbibition of most bio-colloids being very sensitive to changes in the acidity of the medium. It is interesting to note that when bacteria are shaken with distilled water or treated with other coagulating agents the "bacteriophage is spontaneously generated."[3] The coagulating action of distilled water has already been discussed.

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[1] "The Bacteriophage and Its Behavior", 76 (1926); J. Infectious Diseases, 37, 35 (1925); Schweiz. med. Wochenschr., 52, 761 (1922).

The phenomena of drug resistance are well known and are important in bacteriology and medicine. Briefly, it has been found that if organisms are exposed to small amounts of toxic compounds for long periods of time then subjected to a full dose of the toxic agent they are not killed. Every phenomenon from the probability of the survival of the fittest to the loss of the parabasal body in trypanosomes has been used to explain this condition.[4]

Findlay in discussing the problem at the beginning of 1930 says: "It is obvious that at present no satisfactory explanation of drug resistance can be given. It is however, inevitable that the drug resistance which can be required by trypanosomes, spirochaetes, and bacteria, either *in vitro* or *in vivo,* should be compared with the acquired tolerance towards drugs, such as alcohol, exhibited by man." The reason that this problem has been so difficult for the biologists is because the condition is not dependent on biological phenomena. The whole thing is essentially colloidal in nature and is easily explained, including drug tolerance in man. The toxic action of drugs as we have already indicated, depends upon the coagulation of the bio-colloids of the tissue or organ in question; drug tolerance is based upon the well-known phenomena of fractional coagulation.

It is known that in many cases as in hydrated ferric oxide[5] and albumin sols[6] much less of the coagulating agent is required when added all at once than when added in small amounts over a long period of time, particularly when the slow addition causes a partial coagulation of the sol. This fractional precipitate not only removes the coagulating agent by adsorption on the precipitate which in many cases is greater than that of the original sol, but also alters the stability of the sol by decreasing its concentration. Other conditions being equal, a dilute sol, in general, is more stable than a concentrated sol, because the chance that any two particles can come in contact is less. Thus in the treatment of an organism or tissue, with a coagulating drug it need not surprise us that after several small doses the normal toxic dose does not produce the same effect as in the untreated controls, indeed it is rather to be expected. Since there are many sols in a living cell it frequently happens that with two drugs, that are adsorbed upon the same sol, the one drug will make the cell resistant to the other drug. This is due to the fact that the first drug starts the fractional coagulation. In other cases where the two drugs are adsorbed on different sols, the one drug will fail to make the cell resistant to the other drug because it cannot partially coagulate the other sol. The phenomena of drug tolerance which are so difficult to explain on other theories are quite simple when examined in the light of colloid chemistry; it is the natural outcome of the coagulation theory.

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[1] Lloyd: "Chemistry of Proteins".

[2] J. Gen. Physiol., **4**, 245 (1922).

[3] Deutsch. med. Wochenschr., **48**, 383 (1922).

[4] Compt. rend., **153**, 226 (1911); Z. Immunitäts., **43**, 253 (1925).

[5] Z. physik. Chem., **44**, 143 (1903).

[6] Beitr. Chem. Physiol. Path., **5**, 436 (1904).

The colloid theory is based upon the groundwork of logical interpretation of existing data and experimental observation of the colloidal changes with the ultramicroscope. The interpretation of the data in the light of colloidal chemistry must in time become increasingly evident to biological workers that it is not only logical, but flexible enough to cover the great mass of data without any unusual assumptions. In the consideration of this problem nothing but the most elementary facts and assumptions of colloid chemistry have been employed, yet this theory is able to account for and unify the most diversified facts in disinfection and antisepsis.

Turning to the experimental observations with the ultramicroscope it behooves us to state the limitations of this instrument. No one instrument or method will illustrate all types of biological coagulations. The study of the changes in viscosity is, perhaps, the ideal method, but in this particular case there are great experimental difficulties. The ultramicroscope affords the easiest method of study, but unfortunately it is not universal in application. The colloid particles of protein sols are practically invisible due to the fact that the index of refraction of the particles and the surrounding medium are nearly the same, and colloid particles in the ultramicroscope are recognized by the reflected light. The coagulated sols are frequently easy to observe because their optical properties are much different, coagulated egg white being a familiar example. However, there are cases where the transformation of sol to gel is not accompanied by any marked or drastic change in optical properties, ie. in gelatine. Heilbrunn, in fact, regards this as of very frequent occurrence and if it were not for his classical studies of the variations in the viscosity we would still be in the dark concerning some of the most important problems of biology. Naturally such changes as these are quite difficult to observe.

The opposite extreme also exists, if the organisms are surrounded by a thick membrane that reflects a large amount of light we will not be able to see within the cell, although the outlines of the organism are plainly visible. Staphylococci apparently belong to this group; even when these organisms are exposed to saturated bichloride of mercury solutions, or steam, the coagulation is barely perceptible.

We do not wish to give the impression, that the ultramicroscope is not a valuable instrument for this type of work. If the ultramicroscope were used as much in biology and bacteriology as the ordinary microscope, most workers would not have failed to observe phenomena that was already familiar to the minds of bacteriologists and colloid chemists.

The conclusions of this study of disinfection in the light of colloid chemistry indicate that antisepsis is merely a state of narcosis, which depends upon the reversible coagulation of the cell colloids; disinfection is brought about by the irreversible coagulation of the cell colloids. The corollary, that coagulation by whatever means will bring about antisepsis or disinfection, also holds and is exemplified by the action of heat, light, distilled water, and mechanical agitation on bacteria.

Summary

(1) Antisepsis and disinfection in bacteria are similar to narcosis and toxic action in the higher organisms.

(2) The decreasing stability of the cell colloids in the initial stages of coagulation is associated with the phenomena of stimulation; the stage of coagulation that is reversible is responsible for the inhibition of the activity or the organism but does not kill them; the state of irreversible coagulation is responsible for the death of the bacteria.

(3) These colloidal changes were observed in living cells and bacteria by means of the ultramicroscope.

(4) Antiseptics and disinfectants, like narcotics, can act in either of two ways, by directly coagulating the cell colloids, or by interfering with some normal function of the cell to such an extent that the accumulated toxic products will cause the coagulation. Phenol is an example of the first case and arsenic derivatives seem to be of the second type.

(5) The mechanism of disinfection consists of two phases, first the adsorption of the drug and secondly, the coagulation of the cell colloids.

(6) Most workers have confused the nature of the second phase of action with that of a chemical reaction because the velocity of disinfection can be expressed by equations that are used to express the velocity of chemical reactions. This confusion is cleared away by showing that these equations are not "specific for chemical reactions" but can also be used, in certain regions, to express the velocity of coagulation and other physical actions.

(7) The difficulties of a chemical concept of disinfection are shown by the inapplicability of the mass action law, lack of stoichiometrical relations and the abnormal temperature coefficients.

(8) The disinfection by lytic agents is discussed and evidence produced to show that coagulation is the initial phase, the digestion follows the coagulation.

(9) The phenomenon of drug tolerance is explained upon the basis of fractional coagulation: the adsorption of the drug by the coagulum and the increased stability of the diluted sol. This does not preclude the possible formation of substances which counteract the action of the drug.

(10) The limitations of the ultramicroscope in the observations depends on the optical properties of the coagulum being such that it reflects the light and the absence of a thick reflecting membrane around the cells.

Cornell University

VAPOR PRESSURES OF SOME HYDROCARBONS

BY ERNEST G. LINDER*

In making a series of vapor pressure measurements for use in an investigation of some electrical properties of hydrocarbons, serious disagreements were found with published data in standard tables, such as the International Critical Tables and the Landolt-Börnstein Tables. The purpose of this note is to give the new data obtained and to indicate the disagreements and likely reason there-for. Data also have been included on some hydrocarbons on which no previous determinations of vapor pressure seem to have been made. The measurements extend over only a rather small temperature range, because it was desired merely to obtain sufficient data to determine the vapor pressure at 0°C.

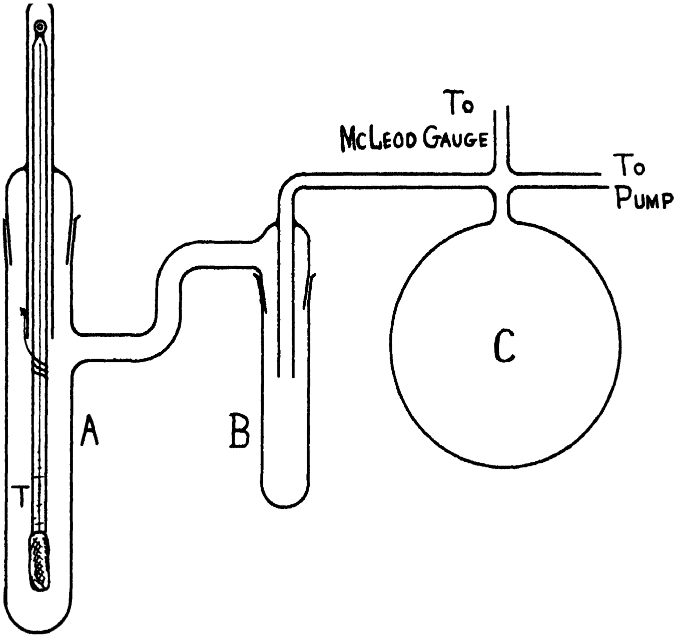

Fig. 1
Vapor Pressure Apparatus

The method used for these measurements was a slight modification of that due to Ramsay and Young.[1] The apparatus is shown in Fig. 1. The essential part is the glass chamber A, containing a thermometer T, with the bulb wrapped with two or three layers of cheesecloth saturated with the hydrocarbon whose vapor pressure is to be measured. B is a trap, cooled either by

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* Research associate, Cornell University. This work is a part of an investigation of organic reactions in electrical discharge, being carried on with a fund maintained by the Detroit Edison Co.

[1] J. Chem. Soc., **47**, 45 (1885).

TABLE I

Vapor Pressure of Hydrocarbons

t°C	V.P. mm Hg.
toluene	
− 9.7	3.53
− 8.7	3.77
− 7.2	4.17
− 4.4	4.98
− 4.35	5 00
− 3.7	5.30
− 3.5	5.36
− 2.75	5.57
tetrahydronaphthalene	
− 2.4	.015
− 1.2	.0235
25.0	.40
65.0	.83
m-xylene	
− 8.4	.90
− 6.75	1.03
− 2.8	1.37
dipentene	
− 5.0	.10
.5	.25
3.3	.31
11.75	.55
14.25	.75
o-xylene	
−17.0	.20
−10.7	.42
.6	1.10
p-xylene	
− 9.5	.33
− 2.5	.87
.2	1.16
ethylbenzene	
−11.6	.56
− 1.2	1.38

t°C	V.P. mm Hg.
mesitylene (E)	
− 1.7	.34
2.3	.50
3.2	.53
n-octane	
− 9.3	1.47
− 3.0	2.32
3.7	3.65
durene	
− 1.7	.013
− 1.3	.016
1.3	.033
1.75	.033?[1]
n-tetradecane	
19	.007—[2]
n-decane	
− 3.8	.165
.2	.21
.5	.23
8.5	.47
n-butylbenzene	
− 4.7	.10
5.5	.25
12.2	.48
sec-butylbenzene	
− 8.6	.10
− 3.0	.18
2.6	.32
9.8	.53

t°C	V.P. mm Hg.
tert-butylbenzene	
− 2.0	.27
2.3	.43
10.8	.82
13.0	1.05?
13.7	1.08
p-diethylbenzene	
− 6.7	.49
− 5.6	.54
− 0.7	.83
6.2	1.35
m-diethylbenzene	
− .8	.15
6.8	.30
10.8	.43
15.7	.74
n-propylbenzene	
− 6.8	.35
− .7	.58
3.6	.85
13.9	1.95
iso-propylbenzene	
− 8.2	.43
1.3	.93
13.7	2.25
octylene	
− 9.0	1.57
− 2.0	2.70
9.5	6.02
di-iso-butylene	
− 9.5	5.12
− 8.3	5.75

TABLE I (Continued)

Vapor Pressure of Hydrocarbons

t°C	V.P. mm Hg.
2-2-4-trimethyl-pentane	
−30.5	1.08
−19.0	2.58
decane (di-iso-amyl)	
− 2.25	.43
.5	.52
5.5	.78
10.3	1.10
hexamethylethane	
−10.3	1.33
− 5.0	2.08?[1]
− .3	3.55
6.0	5.80?
p-menthane	
− 4.9	.32?
2.0	.54
11.8	1.17
p-cymene	
− 5.5	.14
− 5.3	.14
.0	.23
.8	.25
13.3	.68
phenylcyclohexane	
12.4	.017
styrene	
− 7.7	.65
− .5	1.13
8.2	2.16
1-methylcyclohexene	
− 6.5	3.15
− 1.5	5.25
methylcyclohexene	
−26.2	1.30
−17.0	3.19
− 9.6	6.50?
limonene	
− 5.3	.10
2.5	.23
12.2	.54
pinene	
− 6.00	.41
1.00	.72
13.25	1.78
dekahydronaphthalene	
− 4.2	.10
− 0.2	.14
9.5	.32
methylnaphthalene	
14.6	.031
cyclohexene	
−38	.80
diphenylmethane	
19.5	.02−[2]
mesitylene (Kb)	
− 2.75	.29
− 1.20	.33
1.5	.43
10.6	.91
mesitylene (E)	
− 4.2	.28
2.7	.50
10.2	.91
acenaphthene	
20.0	.02−
o-diphenylbenzene	
20.0	.02−

[1] A question mark indicates doubt regarding presence of equilibrium when reading was taken.

[2] A minus sign after a figure indicates that the vapor pressure is less than the given figure.

liquid air or a carbon dioxide-ether slush. Connections are made as shown to a McLeod gauge and vacuum pump. The three-liter flask C increases the volume of the apparatus so that the McLeod gauge can function properly.

In operating the apparatus, the entire system was first pumped down until the thermometer, cooled by the evaporating hydrocarbon, registered a temperature near 0°C. The stopcock to the pump was then closed. After that, sufficient time was allowed for equilibrium to be reached, as indicated by a constant reading of the thermometer. Under equilibrium conditions the part of the system to the left of trap B will be filled with hydrocarbon vapor, whereas nothing but air will be in the portion of the apparatus to the right of B. The air and vapor will be at the same pressure, hence the McLeod gauge will indicate the vapor pressure of the hydrocarbon at the temperature registered by the thermometer.

TABLE II

Vapor Pressures at oC

Substance	from published Tables	Woringer	Linder
water	4.55[1]		4.50
toluene	6.97[1]		6.90
naphthalene	.006[1] .023 .022		.0175
octylene	4.00[2]		3.20
n-decane	.35[2]		.20
p-menthane	.40[2]		.43
dipentene	.30[2]		.25
di-iso-amyl	.70[2]		.50
o-xylene		4.0	1.06
p-xylene		8.29	.95
mesitylene		15.6	.375
ethylbenzene		5.9	1.57
n-propylbenzene		6.25	.60
n-octane	325[2]	4.00	2.95
iso-propylbenzene		6.45	.82

[1] Landolt-Börnstein Tables.
[2] Wilson: Ind. Eng. Chem., 20, 12, 1363 (1928).

This method is especially suited to the measurement of small vapor pressures, where considerable error is frequently committed due to gases absorbed in the liquid. This source of error is entirely absent in the method described here, since any gas given off by the hydrocarbon will be immediately swept over into the chamber C, and become merely a part of the gas contained there-in. Another advantage is that the vapor pressures of solids can be determined. To do this, it is only necessary to remove the cheesecloth wrapping from the thermometer bulb, and coat the bulb by dipping it in the molten hydrocarbon.

The complete data are given in Table I. For some substances, e.g., n-tetradecane, the pump was incapable of reducing the pressure in the system down to the vapor pressure of the substance, hence, for these substances, it can be stated only that the vapor pressure is less than the given figure.

Satisfactory checks of the accuracy of the method were made with water and toluene. These and some other comparisons are given in Table II. Wilson's data were taken from a nomographic chart, and the agreement with the writer's data is very likely within the limits of accuracy of the chart in the region involved, especially since extrapolation on the chart was necessary in some cases.

The writer's data in the last column in the lower part of the table are in serious disagreement with Woringer's data quoted in the other column.[1] Woringer used a static method, i.e., one in which the vapor is contained within a closed space and the pressure measured directly for different fixed temperatures. With such a method small traces of absorbed gases will cause serious errors at low pressures. It seems likely that such an error was present in Woringer's measurements, especially since all his pressures, where there is a disagreement, are greater than the writer's.

In the case of mesitylene (which shows the greatest disagreement) three runs were made by the writer. The first two were made on mesitylene from the Eastman Kodak Company, one being made with carbon dioxide-ether cooling and the other with liquid-air cooling on the trap. Both these runs gave 0.39 mm. of mercury for the vapor pressure at 0° C. The third run was on Kahlbaum mesitylene. This gave 0.36 mm. of mercury. It seems that these figures must be fairly correct.

Summary

For thirty-nine hydrocarbons vapor pressure data in the neighborhood of 0°C. are presented. Some disagreements with published data in standard tables are pointed out and discussed.

The writer wishes to express his appreciation to the Detroit Edison Company for the financial support which has made this investigation possible, and for the permission to publish the data. Thanks are also due to the Physics Department of Cornell University for the laboratory facilities used.

Cornell University,
Ithaca, N. Y.
July, 1930.

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[1] Z. physik. Chem., **34**, 257 (1900).

ACID ADSORPTION AND STABILITY OF NITROCELLULOSE

BY D. R. WIGGAM*

Introduction

It is well known that traces of acid adsorbed by nitrocellulose accelerate its thermal decomposition. The type of acid is unimportant, with the possible exception of the weakest organic acids. The stability is lowered in a degree proportional to the amount of acid adsorbed. The present work has been confined to strong acids, as it is these which are of principal importance to the manufacturer and user of nitrocellulose.

Experimental

The determination of acid adsorption is direct. Two grams of nitrocellulose, dried to constant weight at 70°C., were added to 50 cc. of N/100 acid and allowed to stand for 15-30 minutes with occasional stirring. Longer standing was not found necessary. An aliquot was withdrawn and titrated with standard base, using methyl orange as the indicator. The reading of the endpoint at these dilutions requires some practice but becomes quite precise after a few trials. Base consumption by the sample was carried out in an analogous manner. Adsorptions are reported as cubic centimeters of N/100 acid used up per gram of nitrocellulose.

Thermal decomposition was followed by the 134.5°C. methyl violet test. Two and five-tenths gram samples of oven-dry (70°C.) nitrocellulose are placed in special test tubes and tamped tightly. A methyl violet test paper is placed in the tube above the nitrocellulose and the mouth of the tube plugged with a perforated stopper. The tube is placed in a special constant temperature bath at 134.5°C. and heated until the paper has completely changed color to a salmon pink. The time required for this change in color is reported.

Two types of nitrocellulose were first studied, designated as 5119 with nitrogen content 13.09 per cent and 4200 with nitrogen content 13.47 per cent. These are smokeless powder types, and in the process of manufacture had been reduced to pulverulent condition. They were stabilized by usual methods of processing.

With sulfuric, nitric and hydrochloric acids, adsorption data are given in Table I.

Experiments 1, 2 and 3 indicate how closely the results of successive determinations checked. Sulfuric and nitric acids are adsorbed to the same degree; hydrochloric acid somewhat less.

The two nitrocelluloses were suspended in N/100 NaOH. Aliquots of the supernatant liquid were removed and titrated with acid. Three one-hundredths cc. N/100 NaOH were used up per gram of sample by 5119, and

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*Hercules Powder Company.

TABLE I

A = cc. N/100 acid adsorbed per gm. N.C.

Exp. No.	N.C.	Acid	A	Exp. No.	N.C.	Acid	A
1	5119	H_2SO_4	0.44	5	5119	HCl	0.41
2	5119	”	0.46	6	4200	H_2SO_4	0.37
3	5119	”	0.45	7	4200	HNO_3	0.36
4	5119	HNO_3	0.46	8	4200	HCl	0.29

0.12 cc. N/100 NaOH were used up per gram by 4200. Faint traces of acid may be present on nitrocellulose from incomplete removal in its preparation or from incipient thermal decomposition on drying. At ordinary storage temperatures with moist material the latter reaction has almost zero rate.

If the residual adsorbed acid had been removed before suspending in acid, the adsorptions would have been as follows:

H_2SO_4 − 0.45 + 0.03 = 0.48 cc./gm. 5119
HNO_3 − 0.46 + 0.03 = 0.49 ” ” ”
HCl − 0.41 + 0.03 = 0.44 ” ” ”
H_2SO_4 − 0.37 + 0.12 = 0.49 ” ” 4200
HNO_3 − 0.36 + 0.12 = 0.48 ” ” ”
HCl − 0.29 + 0.12 = 0.41 ” ” ”

To verify the above results, samples of 5119 and 4200 were enclosed in semi-permeable nitrocellulose membranes and suspended for 30 days in distilled water, which was replaced continuously. No. 5119 then adsorbed 0.51 cc. N/100 sulfuric acid and 4200 adsorbed 0.50 cc. N/100 acid. The results agree within the limit of accuracy of the method.

Adsorptions were determined in the above manner on two further samples of nitrocellulose of different nitrogen contents. (Table II), No. 734 was long-fibre material of nitrogen 12.15 per cent, No. 4467 was pulverulent, with 12.86 per cent nitrogen.

TABLE II

A = cc. N/100 acid adsorbed per gm. N.C.

N.C.	Acid	A	N.C.	Acid	A
734	H_2SO_4	0.87	4467	H_2SO_4	0.36
734	HNO_3	0.88	4467	HNO_3	0.38
734	HCl	0.66	4467	HCl	0.34

The results follow, in general, the same trend as shown with the higher nitrogen samples. Base consumptions for the above samples showed that 0.58 cc. N/100 base were required per gram of 734 and 0.54 cc. for 4467. Had the samples been purified by dialysis the sulfuric acid adsorptions would have been,

734..........0.87 + 0.58 = 1.45 cc.
4467..........0.36 + 0.54 = 0.90 cc.

The total acid adsorption is thus dependent on the nitrogen content of the nitrocellulose. The total surface of the individual samples of nitrocellulose was not determined. The specific surface would vary from sample to sample, due to different degrees of pulping, but for any one sample would be substantially constant.

Known amounts of acids were deposited on nitrocelluloses 5119 and 4200, and the stabilities determined by the methyl violet test. After suspension in N/100 acid, the sample was filtered on a Buchner funnel and sucked as dry as possible. It was then stirred into 1000 cc. distilled water and agitated for several minutes, filtered and dried. Acid adsorptions were run with sulfuric, nitric and hydrochloric acids. Knowing the total adsorptive capacities from previous data, the retained acid could be calculated. Table IV gives this data, together with the methyl violet heat tests.

TABLE IV

N.C.	Kind of Acid	cc. N/100 Acid Ads. after Treatment	cc.N/100 Acid Ret'd.	Methyl Violet Test
5119	Original*	—	0.03	28 Min.
5119	H_2SO_4	0.20	0.29	26½ "
5119	H_2SO_4	0.32	0.16	27 "
5119	HNO_3	0.08	0.40	26½ "
5119	HCl	0.13	0.31	26½ "
4200	Original*	—	0.12	27½ "
4200	H_2SO_4	0.25	0.24	25 "

* This refers to untreated sample. Retained acid may be nitric or sulfuric or both.

Traces of free acid have a distinct effect in lowering the methyl violet test. In spite of their greater volatility at the temperature of the test, hydrochloric and nitric acid, when adsorbed, have approximately the same effect as sulfuric in lowering stability of nitrocellulose. None of the samples exploded in five hours in the bath.

Larger amounts of sulfuric acid were deposited on nitrocellulose by evaporation of dilute acid solutions in contact with 5119 at low temperature. After drying, the stabilities were determined by the methyl violet test. The results are given in Table V and Fig. 1.

TABLE V

Equivalent Vol. of N/100 Acid/Gm. N.C.	Mols Acid/Gm. N.C.	Methyl Violet Test	Explosion Time
4.793	0.00004793	5½ Min.	19 Min.
2.647	0.00002647	7 "	45 "
1.178	0.00001178	8½ "	5 + Hrs.
1.096	0.00001096	8¾ Min.	5 + Hrs.
0.649	0.00000649	10¼ "	5 + Hrs.
0.29 *	0.0000029	26½ "	5 + Hrs.

* From Table IV.

If the acid adsorbed is of the order of 3×10^{-6} mols. per gram of nitrocellulose or less, the effect on the resistance to decomposition (stability) is not serious. It should be noted that this figure applies only to high nitrogen content nitrocellulose for use in smokeless powder. For the lower nitrogen content nitrocelluloses, much larger amounts of acid would be required to have a proportionate effect.

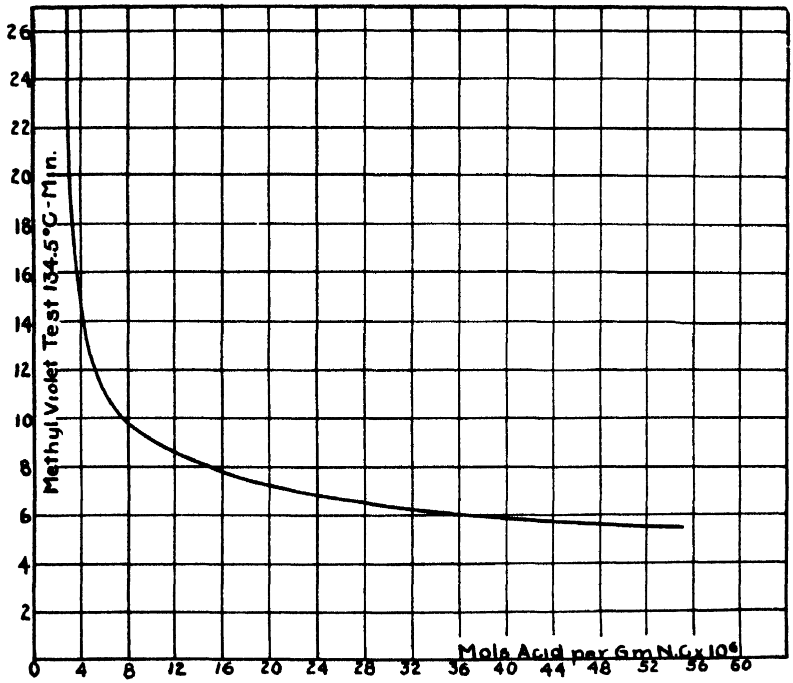

FIG. 1
Effect of adsorbed Acid on Stability

Summary

At the dilutions used in this work, nitric and sulfuric acids are adsorbed to approximately the same extent, while hydrochloric acid is adsorbed to a somewhat lesser degree. Base adsorption by nitrocellulose apparently does not take place. When nitrocellulose is dipped in dilute base, some of the latter is used up to neutralize the acid present on the fibre, accounting for an apparent adsorption. When this acid is removed by dialysis, the acid adsorption becomes equal to the acid plus base consumption of undialyzed fibre.

Acid retained by the fibre lowers the resistance to heating of nitrocellulose with a given sample. The effect of equal amounts of the three strong acids used lowered the heat resistance to approximately the same degree. A smooth curve is obtained by plotting the results of the methyl violet test (stability) against the acid adsorption.

NEPHELOMETRIC TITRATIONS. I. THE EQUAL-OPALESCENCE END-POINT*

One of the outstanding procedures now in use in the determination of exact atomic weights is the so-called "nephelometric method" of titration. The general method consists in estimating the stoichiometrical ratio between a pure compound furnishing chloride or bromide ions, and pure silver, with the use of the nephelometer.

This method was first used by Richards and Wells[1] in 1905 to determine the NaCl:Ag ratio, from which the atomic weight of sodium may be calculated, by taking suitable values of the antecedent atomic weights of chlorine and silver. The method has subsequently been applied to the analysis of other chlorides and bromides, to determine the atomic weights of many elements. In these analyses, the procedure described by Richards and Wells has been used without essential modification, in determining the end-point of the nephelometric titrations (the equal-opalescence end-point).

At the present time the accepted values of a large number of atomic weights rest almost entirely upon ratios determined by the nephelometric method. This is in part due to the convenience and simplicity of the method; it has been preferred by investigators who have used modern methods to prepare pure compounds for atomic weight analysis. Furthermore, the "probable error" of atomic weights calculated from ratios determined nephelometrically is rather generally lower than the "probable error" of corresponding values calculated from ratios found by other chemical methods. In short, there has developed a tendency toward giving "nephelometric" values preference over the values obtained by other methods, which are regarded mainly for the confirmatory evidence which they furnish.

Curiously enough, in view of the wide application of the nephelometric method in atomic weight work, and the general reliance placed on "nephelometric" results, there have been few attempts to demonstrate the unqualified applicability of the method in the case of particular analyses. Richards and Wells, in a series of tests which showed the applicability of the method to the NaCl:Ag titration, established the essential soundness of the equal-opalescence end-point. Nevertheless, there are certain features of this end-point which make it seem desirable to extend the experiments of Richards and Wells, more particularly to titrations in which multivalent ions are present in the analytical solutions.

In the titrations under consideration, an acid solution containing the chloride or bromide ions from a weighed quantity of a pure compound is precipitated with almost the theoretical amount of pure silver, weighed, and dissolved in nitric acid. The titration consists in adjusting to equality the silver and halide ions in the resulting supernatant solution, by the use of standard silver and halide solutions. In the equal-opalescence method, this adjustment is based on nephelometric tests which, presumably, show the *relative* amounts of silver and halide ions in the solution.

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*Contribution from the Chemistry Department of The Rice Institute.

**National Research Fellow in Chemistry.

[1] Richards and Wells: J. Am. Chem. Soc., 27, 502 (1905).

The end-point of each titration, and hence the calculated atomic weight, depends upon the comparison of two colloidal suspensions of silver chloride. These suspensions are formed in equal samples of the supernatant analytical solution, in two matched test-tubes, under conditions as nearly identical as possible. Silver nitrate is added in excess to one tube. An equivalent excess of a suitable alkali halide is added to the other tube, so that, according to the "solubility product" principle, one suspension represents practically all of the silver ions, the other practically all of the chloride ions present in the supernatant analytical liquid. At the stoichiometrical point, the numbers of silver and halide ions in the supernatant liquid are, supposedly, equal. If, from a solution at the stoichiometrical point, the above procedure results in the production of two suspensions possessing equal light-reflecting power during the time required for the nephelometric observations, the desired correspondence between the end-point and the stoichiometrical point is attained. In this case the opalescences in the two tubes are equal, and the two parts of the divided field seen through the nephelometer eyepiece are the same, when the ratio of the exposed lengths of the tubes is 1.00.

In every equal-opalescence titration, in spite of the attempt to compare the silver chloride suspensions under exactly similar conditions, there must be at least one very marked difference in the two sols. One, stabilized by the adsorption of excess Cl^- ions, is negative; the other, stabilized by the adsorption of excess Ag^+ ions, is positive[1]. Experiments may be cited to show that under certain special conditions this dissimilarity introduces no error into the nephelometric readings. For example, Richards and Wells[2] demonstrated that the "extra" ions present in the analytical solutions had no effect upon the end-point of the NaCl:Ag titration. Scott and Johnson[3] tested five saturated solutions of silver chloride containing varying amounts of nitric acid and found no deviation from equality of silver and chloride ions which would affect even the most accurate atomic weight analyses.

For the present purpose, it seems desirable to emphasize the fact that the ions involved in the above-mentioned tests were all univalent. In other atomic weight determinations, "extra" ions of the most widely varied character, di-, tri-, and tetravalent, derived from the compounds undergoing analysis, have been present in the test solutions examined in the nephelometer. The effect of the adsorption of these ions upon the quantity, state of division, structure, color, and stability of the sols (i.e., upon their light-reflecting power) cannot certainly be stated. However, it is known that the coagulating power of some ions is hundreds of times greater than that of other ions. Furthermore, any given ion is more likely to affect a sol of opposite charge than one having the same charge[1]. Only rarely, then, would one expect the action of any particular "extra" ion to be equal in the two nephelometer tubes,—in most cases its effect upon the properties of the two oppositely charged colloidal suspensions should be different.

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[1] Lottermoser: J. prakt. Chem., (2) **72**, 39 (1905); **73**, 374 (1906).

[2] Richards and Wells: J. Am. Chem. Soc., **27**, 503 (1905).

[3] Scott and Johnson: J. Phys. Chem., **33**, 1981 (1929).

The good general agreement between atomic weights determined nephelometrically and corresponding values determined by other methods insures that the effect under consideration must be small. Nevertheless, one would be unjustified in assuming that the effect is negligible. The nephelometer, as Richards and Wells[2] have often pointed out, is an extremely sensitive instrument. It seems very likely that the unbalanced action of certain ions (mainly multivalent ions) may cause differences in the light-reflecting power of the sols large enough to produce serious constant errors in the nephelometric observations.

There is nothing in the procedures described in reports of atomic weight titrations to assure one that the above-mentioned source of error has been avoided. The conditions (temperature, time after precipitation, etc.) under which the suspensions of silver chloride are compared in nephelometric titrations are really quite arbitrary, although they depend more or less upon the "solubility product" idea. In most cases it has been customary to compare the suspensions at the equilibrium condition which most facilitates the nephelometric observations. Since the equilibrium is influenced by factors which the "solubility product" rule does not take into account, the point of equal opalescence in any given titration may or may not correspond to the stoichiometrical point. Under the circumstances, one may reasonably question the unqualified general applicability of the equal-opalescence end-point to extremely accurate titrations. Only applications based on experiments such as those described by Richards and Wells would appear to be entirely trustworthy; the procedure should be tested for each analysis.

Some preliminary tests, made in this laboratory, indicate that a small effect exists, and emphasize the need for further experiments, which are to be undertaken at Princeton University, under a grant from the National Research Council.

Summary

A possible source of error in the equal-opalescence end-point used in nephelometric atomic weight titrations has been pointed out. The nature of the possible error suggests the advisability of testing some of the more general applications of the original procedure described by Richards and Wells.

The writer wishes to acknowledge his indebtedness to Dr. H. B. Weiser and to Dr. A. F. Scott for suggestions concerning this article.

Houston, Texas.

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[1] Schulze: J. prakt. Chem., (2) **25**, 431 (1882); **27**, 320 (1883).

[2] Richards and Wells: Am. Chem. J., **31**, 239, 241, 242 (1904); J. Am. Chem. Soc., **27**, 486 (1905).

THE MECHANISM OF THE MUTUAL COAGULATION PROCESS

BY HARRY B. WEISER AND THOMAS S. CHAPMAN

When suitable amounts of two sols of opposite sign are mixed, complete mutual coagulation takes place.[1] This is ordinarily attributed to the mutual discharge of the electrically charged particles of opposite sign with subsequent agglomeration into clumps that settle out. The observations of Biltz are commonly cited to show that the action is determined only by the charge on the particles and not at all on their nature.[2] Thus a comparison of the precipitating action of a series of sols is said to disclose that while the optimum amount of positive sols required to precipitate negative sols varies, the order is always the same. Bancroft[3] pointed out that this deduction from Biltz's data is not justified. Wintgen and Löwenthal[4] state the generally accepted view in another way when they say that the mutual precipitation of oppositely charged sols is a maximum when the concentrations of the sols expressed in equivalent aggregates are the same, that is, when equal numbers of charges of opposite sign are mixed. This rule was likewise found not to hold when a highly dispersed sol of one sign is mixed with a coarser sol of opposite sign.

Lottermoser[5] observed that the most complete coagulation of positively charged AgI containing a slight excess of $AgNO_3$ and negatively charged AgI containing a slight excess of KI, was obtained when the excess of $AgNO_3$ in one sol is just equivalent to the excess of KI in the other. This suggests that interaction between the stabilizing ions is the cause of the mutual coagulation of oppositely charged sols. In line with this Freundlich and Nathansohn[6] found colloidal As_2S_3 sol and Odén's sulfur sol to be instable in the presence of each other. Since both sols are negatively charged, this instability cannot be due to mutual electrical neutralization but was found to result from interaction between the stabilizing electrolytes of the two sols, hydrogen sulfide and pentathionic acid. Following up the above observations, Thomas and Johnson[7] attribute mutual coagulation in other cases primarily to chemical interaction of the stabilizing electrolytes in the sols. Thus, the precipitation of Graham's colloidal ferric oxide, stabilized by hydrogen ion, and colloidal silica, stabilized by hydroxyl ion, was attributed to chemical neutralization. This view was supported by the observation that mutual precipitation was effected over a limited range of purity of sols, when the hydrochloric acid and sodium hydroxide concentration in the sols were approximately equivalent. The variation from equivalence was quite marked in case the sols were fairly pure. Thus a silica sol containing 16 SiO_2 to 1 NaOH was precipitated at various dilutions with a sol containing 13 Fe_2O_3 to 1 $FeCl_3$. At the highest dilution possible for obtaining accurate data, mutual precipitation was observed when an amount of colloidal silica was added corresponding to but 50 per cent of the hydrochloric acid. This variation was attributed to the metastability of pure sols, which causes them to precipitate with a subnormal disturbance. This does not seem quite convincing since, in the absence of contamination other than that mentioned, the purity of the sols would scarcely be great enough to make them abnormally sensitive. Erratic results were also obtained when the amount of peptizing agent was too large, say three times as much as in the case referred to above. Thus, to obtain data to support a purely chemical mechanism involving neutralization of the stabilizing agents, it seems necessary to choose the experimental conditions to fit the case. While everyone will agree that the peptizing agents of two sols may interact under certain conditions, thus affecting the stability of each, such a mechanism of the mutual precipitation process would not account for the repeated observation of mutual precipitation of sols where interaction between the peptizing agents is impossible or improbable.[1] In an attempt to throw some further light on the several factors which influence the mutual coagulation process, the experiments reported in this paper were carried out.

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[1] Graham: J. Chem. Soc., **15**, 246 (1862); Linder and Picton: **71**, 586 (1897); Henri: Compt. rend. Soc. biol., **55**, 1666 (1903); Bechhold: Z. physik. Chem., **48**, 385 (1904); Neisser and Friedman: Münch. Med. Wochenchr., **51**, 465, 827 (1904); Biltz: Ber., **37**, 1095 (1904); Billitzer: Z. physik. Chem., **51**, 148 (1905); Teague and Buxton: **60**, 489 (1907).

[2] Freundlich: "Kapillarchemie," 402 (1909); Thomas: Bogue's "Colloidal Behavior," **1**, 325 (1924).

[3] J. Phys. Chem., **19**, 362 (1915).

[4] Z. physik. Chem., **109**, 391 (1924).

[5] Kolloid-Z., **6**, 78 (1910).

[6] Kolloid-Z., **28**, 258 (1920); **29**, 16 (1921).

[7] J. Am. Chem. Soc., **45**, 2532 (1923).

Preparation of Sols

Most of the sols used in this investigation were prepared by standard methods which in many cases have been modified by procedures already described in detail. To avoid repetition, the sols employed are listed in Table I together with references which give the details of the method of preparation used in each case. In general it may be said that special precautions were taken in the preparation of the sols. Chemicals of a high degree of purity were used and all operations were carried out in pyrex vessels. In every case with the exception of the night blue sol, the preparations were subjected to prolonged dialysis in Neidle[2] dialyzers using cellophane bags.

Two series of experiments were carried out with a six-month interval between. The sols were freshly prepared for each series. The concentrations in grams per liter of the sols used in getting quantitative mutual coagulation data are included in Table I. These values were obtained by evaporating a known volume of sol to dryness in a platinum dish, and weighing the residue after suitable ignition.

The zinc and copper ferrocyanide sols used in the first series of experiments were prepared by the interaction of hydroferrocyanic acid and copper salt

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[1] Thomas questions whether any such cases exist: J. Chem. Education, 4, 418 (1927).

[2] J. Am. Chem. Soc., 38, 1270 (1916).

TABLE I

Sols used in Mutual Coagulation Experiments

Sol	Reference to Method of Preparation	Concentration g per l	
		I	II
As_2S_3	Freundlich and Nathansohn: Kolloid-Z., **28**, 258 (1928).	2.22	1.64
SnO_2	Weiser: J. Phys. Chem., **26**, 682 (1922).	2.37	1.73
Congo red acid	Weiser and Radcliffe: J. Phys. Chem., **32**, 1878 (1928).	1.95	0.61
$Cu_2Fe(CN)_6$	Weiser: J. Phys. Chem., **30**, 1530 (1926).	3.28	3.23
$Zn_2Fe(CN)_6$	Same procedure as for $Cu_2Fe(CN)_6$ sol.	2.10	—
Sulfur	Weiser and Cunningham: Colloid Symposium Monograph, **6**, 326 (1928).	—	0.30
Molybdenum blue	Biltz: Ber., **35**, 4431 (1902).	—	0.18
Night blue	Addition to water	—	0.72
$Fe_2O_3(-)$	Hazel and Sorum: J. Am. Chem. Soc., **52**, 1337 (1930).	—	0.30
$Fe_2O_3(+)$	Sorum: J. Am. Chem. Soc., **50**, 1263 (1928).	2.59	1.72
Cr_2O_3	Neidle: J. Am. Chem. Soc., **39**, 71 (1917).	2.17	0.82
CeO_2	Biltz: Ber., **35**, 4431 (1902).	2.50	—
$BaSO_4$	Modification of Kato's method. See below.	14.79	5.60
$BaCO_3$	Buzagh: Kolloid-Z., **38**, 222; **39**, 218 (1926).		
Sb_2S_3	Biltz: Ber., **37**, 1097 (1904).		
$Cu_3(FeC_6N_6)_2$	See below.		
$AgI(-)$	Lottermoser: J. prakt Chem., (2) **68**, 340 (1903).		
$TlI(+)$	Ostwald: "Die wissenschaftlichen Grundlagen der analytischen Chemie," 209 (1904).		

while in the later experiments potassium ferricyanide was employed. The use of hydroferrocyanic acid to obtain the salt is advantageous since the precipitate is almost pure $Cu_2Fe(CN)_6$.[1]

Copper ferricyanide sol was prepared by mixing equivalent amounts of dilute solutions of potassium ferricyanide and copper sulfate, followed by washing the precipitated gel in the centrifuge until peptization was complete and dialyzing.

The colloidal barium sulfate used in the first series of experiments was prepared by the method of Kato[2] which consists in diluting a 1 molar solution of sulfuric acid with twice its volume of alcohol and adding to it an equivalent amount of a molar solution of barium acetate diluted with 5 times its volume of alcohol. The resulting gelatinous precipitate and milky sol were evaporated to dryness under reduced pressure below 40° and the precipitate was dispersed by shaking with water. Due to the difficulty of removing the acetic

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[1] Cf. Weiser: J. Phys. Chem., **34**, 343 (1930).

[2] Mem. Coll. Sci. Kyoto Imp. Univ., **2**, 187 (1909-10).

TABLE II

Mutual Coagulation of Oppositely Charged Sols

Positive Sol	Stabilizing Ion	Negative Sol	Stabilizing ion Ion	Remarks
Fe_2O_3 (Sorum)	$H^{\cdot}$	$Zn_2Fe(CN)_6$	$Fe(CN)_6''''$	$H_4Fe(CN)_6$ soluble and highly ionized
$BaCO_3$	$Ba^{\cdot\cdot}$	$Zn_2Fe(CN)_6$	$Fe(CN)_6''''$	$Ba_2Fe(CN)_6$ quite soluble
$BaSO_4$	$Ba^{\cdot\cdot}$ and $H^{\cdot}$	$Cu_2Fe(CN)_6$	$Fe(CN)_6''''$	$Ba_2Fe(CN)_6$ and $H_4Fe(CN)_6$ soluble
$BaCO_3$	$Ba^{\cdot\cdot}$	SnO_2	OH'	$Ba(OH)_2$ soluble
$BaCO_3$	$Ba^{\cdot\cdot}$	As_2S_3	HS'	BaHS soluble
Fe_2O_3 (Graham)	$H^{\cdot}$ and $Fe^{\cdot\cdot\cdot}$	$Cu_3(FeC_6N_6)_2$	$Fe(CN)_6'''$	$H_3Fe(CN)_6$ and $Fe(FeC_6N_6)$ soluble
Fe_2O_3 (Sorum)	$H^{\cdot}$	Congo red acid	Congo red anion	pH of Fe_2O_3 sol 6.8.
$BaSO_4$	$Ba^{\cdot\cdot}$ and $H^{\cdot}$	$Cu_3(FeC_6N_6)_2$	$Fe(CN)_6'''$	$Ba_3(FeC_6N_6)_2$ and $H_3Fe(CN)_6$ soluble
TlI	$Tl^{\cdot}$	SnO_2	OH'	TlOH soluble
$BaCO_3$	$Ba^{\cdot\cdot}$	AgI	I'	BaI_2 soluble

acid by this method, the sol used in the second series of experiments was prepared by mixing alcoholic sulfuric acid with a slight excess of alcoholic barium acetate, followed by dialysis. This procedure served to replace the alcohol with water and to remove the acetic acid giving a sol which has stood for two months without coagulating.

The Question of Interaction of Stabilizing Ions in Mutual Coagulation

If the stabilizing ions of two oppositely charged sols are capable of interacting to form an insoluble or a slightly dissociated compound it is altogether likely that such interaction will influence the mutual coagulation process. Thus, interaction between the stabilizing hydrogen and ferric ions in a Graham ferric oxide sol and the hydroxyl ions in a silicon dioxide sol will influence the mutual coagulation of the two sols as emphasized by Thomas and Johnson.[1] But mutual coagulation in general is not dependent on the removal of the respective stabilizing ions by such an interaction. This is illustrated by the results of some observations on the mutual coagulation of oppositely charged sols where there is no interaction between the stabilizing ions with the formation of an insoluble or slightly dissociated compound. In these experiments a 10 cc portion of one sol was taken and the other sol was added quite slowly until a point of complete mutual coagulation was found. A few combinations are recorded in Table II. The list may be extended by anyone who desires.

Quantitative Observations of Mutual Coagulation

First Series. The procedure employed in the first series of experiments was as follows: A suitable volume of one sol was taken and varying amounts of a second sol of opposite sign was added until the approximate range of complete mutual coagulation was located. The zone of complete coagulation was then determined more sharply by making a series of mixtures in the boundary region using a constant volume of one sol and slightly varying amounts of the second. The mixtures were allowed to stand 30 minutes after which they were centrifuged for 1 minute at 3000 r.p.m. in a No. 1 International-Equipment-Company centrifuge and examined for complete coagulation. When the presence of a small amount of colloid was not readily determined by visual observation as in the case of stannic oxide sol, a portion of the supernatant liquid after centrifuging was pipetted off and treated with an electrolyte containing a multivalent precipitating ion. The absence of a precipitate or floc on standing two hours was taken as an indication that no sol was present. The results are given in Tables III, IV, V, and VI.

The results recorded in Tables III to VI are represented in a diagram, Fig. 1. The right hand side of the diagram corresponds to 100 per cent by weight of Cr_2O_3, CeO_2, Fe_2O_3, and $BaSO_4$, respectively, and 0 per cent of As_2S_3, $Cu_2Fe(CN)_6$, Congo red acid, SnO_2, and $Zn_2Fe(CN)_6$; while the left hand side corresponds to 100 per cent of the latter compounds and zero per

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[1] Loc. cit.

TABLE III

Mutual Coagulation of Fe_2O_3 Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Fe_2O_3 by weight[1]
Fe_2O_3	SnO_2	10	1.6	10	1.8	10	2.0	10	2 2	86.0 to 84.5
Fe_2O_3	$Zn_2Fe(CN)_6$	10	1.2	10	1.4	10	4.0	10	4.2	90.0 to 75.5
Fe_2O_3	$Cu_2Fe(CN)_6$	5	1.0	5	1.25	5	2.0	5	2.25	76.0 to 66.5
Fe_2O_3	Congo red acid	5	1.5	5	1.75	5	4.75	5	5.0	79.0 to 58.0
Fe_2O_3	As_2S_3	5	5.0	5	4.25	5	6.0	5	6.25	57.5 to 49.0

[1] The concentrations of the several sols are given in Table I.

TABLE IV

Mutual Coagulation of Cr_2O_3 Sol and Negative Sols.

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Cr_2O_3 by weight
Cr_2O_3	$Zn_2Fe(CN)_6$	5	6.0	2	2.5	2	6.5	2	6.75	45.5 to 24.0
Cr_2O_3	SnO_2	2	3.75	2	4.0	2	6.0	2	6.25	31.5 to 23.5
Cr_2O_3	Congo red acid	1	5.75	1	6.0	1	6.75	1	7.0	15.5 to 14.0
Cr_2O_3	$Cu_2Fe(CN)_6$	1	5.0	1	5.25	1	7.75	1	8.0	11.0 to 7.5
Cr_2O_3	As_2S_3	1	11.5	1	11.75	1	15.0	1	15.25	7.5 to 6.0

TABLE V

Mutual Coagulation of CeO_2 Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% CeO_2 by weight
CeO_2	$Zn_2Fe(CN)_6$	5	3.50	5	3.75	5	5.00	5	5.25	61.0 to 54.5
CeO_2	SnO_2	5	4.00	5	4.25	5	5.00	4.75	5.00	55.0 to 51.5
CeO_2	As_2S_3	3	1.50	3	1.75	3	11.00	3	12.00	66.0 to 23.5
CeO_2	Congo red acid	3	5.25	3	5.50	3	9.00	3	9.25	41.0 to 30.0
CeO_2	$Cu_2Fe(CN)_6$	3	4 25	3	4.50	3	6.75	3	7.00	39.0 to 25.0

TABLE VI

Mutual Coagulation of $BaSO_4$ Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% $BaSO_4$ by weight
$BaSO_3$	Congo red acid	5	1.50	5	1.75	5	6.00	5	6.25	95.5 to 86.5
$BaSO_4$	As_2S_3	5	3.00	5	3 25	5	4.25	5	4.5	91.0 to 89.0
$BaSO_4$	$Cu_2Fe(CN)_6$	5	1.25	5	1.50	5	3.75	5	4.0	94 0 to 86.0
$BaSO_4$	$Zn_2Fe(CN)_6$	5	4.00	5	4.25	5	6.00	5	6.25	89.0 to 85.5
$BaSO_4$	SnO_2	5	3 00	5	3.25	5	8.00	5	8.25	90.5 to 79.5

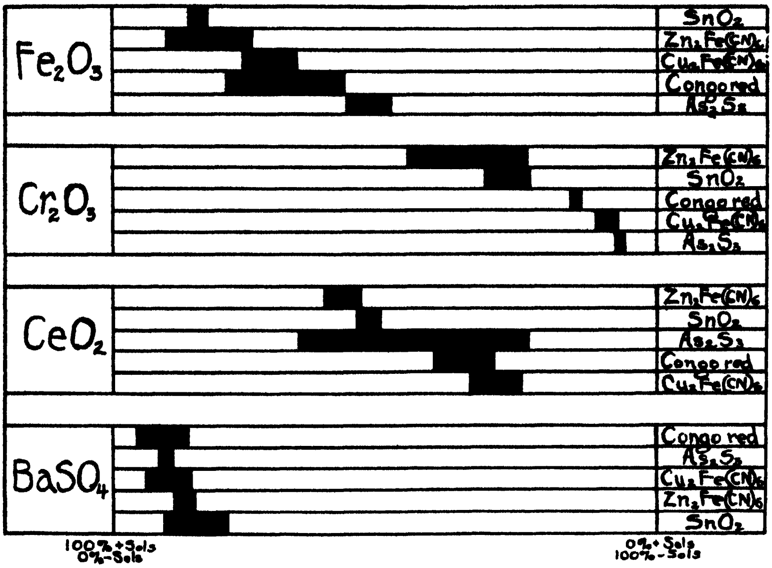

FIG. 1

Range of mutual coagulation of oppositely charged sols. Series I.

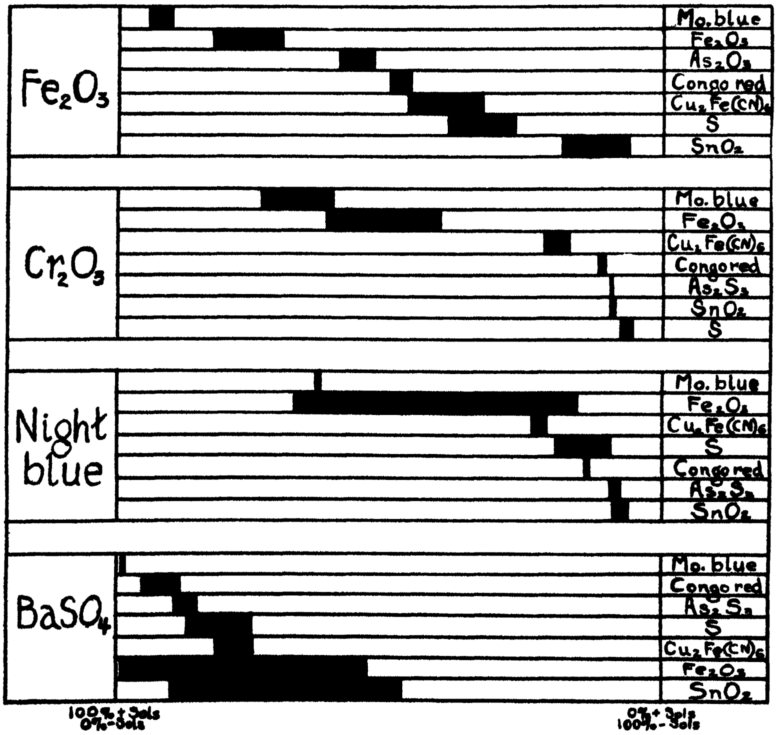

FIG. 2

Range of mutual coagulation of oppositely charged sols. Series 2.

TABLE VII

Mutual Coagulation of Fe_2O_3 Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Fe_2O_3 by weight
Fe_2O_3	Molybdenum blue	4.8	5.2	4.9	5.1	6.3	3.7	6.4	3.6	94.2 to 90.2
Fe_2O_3	Fe_2O_3	2.8	7.2	2.9	7.1	4.5	5.5	4.6	5.4	82.5 to 70.0
Fe_2O_3	As_2S_3	5.1	4.9	5.2	4.8	5.8	4.2	5.9	4.1	59.1 to 53.2
Fe_2O_3	Congo red acid	2.2	7.8	2.3	7.7	2.6	7.4	2.7	7.3	49.8 to 45.8
Fe_2O_3	$Cu_2Fe(CN)_6$	4.7	5.3	4.8	5.2	6.2	3.8	6.3	3.7	46.5 to 32.9
Fe_2O_3	Sulfur	0.5	9.5	0.6	9.4	1.0	9.0	1.1	8.9	39.0 to 27.0
Fe_2O_3	SnO_2	0.5	9.5	0.6	9.4	1.8	8.2	1.9	8.1	18.0 to 6.0

TABLE VIII

Mutual Coagulation of Cr_2O_3 Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Cr_2O_3 by weight
Cr_2O_3	Molybdenum blue	2.4	7.6	2.5	7.5	3.8	6.2	3.9	6.1	73.6 to 60.3
Cr_2O_3	Fe_2O_3	1.9	8.1	2.0	8.0	3.7	6.3	3.8	6.2	61.6 to 40.5
Cr_2O_3	$Cu_2Fe(CN)_6$	4.4	5.6	4.5	5.5	5.2	4.8	5.3	4.7	21.6 to 17.2
Cr_2O_3	Congo red acid	0.7	9.3	0.8	9.2	0.9	9.1	1.0	9.0	11.7 to 10.5
Cr_2O_3	As_2S_3	1.5	8.5	1.6	8.4	1.7	8.3	1.8	8.2	9.4 to 8.7
Cr_2O_3	SnO_2	1.5	8.5	1.6	8.4	1.8	8.2	1.9	8.1	9.4 to 8.2
Cr_2O_3	Sulfur	0.1	9.9	0.2	9.8	0.3	9.7	0.35	9.65	7.8 to 5.3

TABLE IX

Mutual Coagulation of Night Blue Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Fe_2O_3 by weight
Night blue	Molybdenum blue	2.8	7.2	2.9	7.1	3.0	7.0	3.1	6.9	63.0 to 62.0
Night blue	Fe_2O_3	0.6	9.4	0.7	9.3	4.6	5.4	4.7	5.3	67.2 to 15.3
Night blue	$Cu_2Fe(CN)_6$	5.3	4.7	5.4	4.6	5.8	4.2	5.9	4.1	23.5 to 20.7
Night blue	Sulfur	0.3	9.7	0.4	9.6	0.9	9.1	1.0	9.0	19.2 to 9.1
Night blue	Congo red acid	1.0	9.0	1.1	8.9	1.2	8.8	1.3	8.7	13.8 to 12.7
Night blue	As_2S_3	1.4	8.6	1.5	8.5	1.8	8.2	1.9	8.1	8.8 to 7.2
Night blue	SnO_2	1.2	8.8	1.3	8.7	1.8	8.2	1.9	8.1	8.4 to 5.9

TABLE X

Mutual Coagulation of $BaSO_4$ Sol and Negative Sols

Sols mixed		Observations with mixtures								Range of mutual coagulation
		Excess positive sol		Complete mutual coagulation		Complete mutual coagulation		Excess negative sol		
+	−	cc +	cc −	cc +	cc −	cc +	cc −	cc +	cc −	% Fe_2O_3 by weight
$BaSO_4$	Molybdenum blue	6.3	3.7	6.4	3.6	7.8	2.2	7.9	2.1	99.1 to 98.2
$BaSO_4$	Congo red acid	4.3	5.7	4.4	5.6	6.6	3.4	6.7	3.3	94.8 to 87.8
$BaSO_4$	As_2S_3	6.2	3.8	6.3	3.7	7.1	2.9	7.2	2.8	89.3 to 85.3
$BaSO_4$	Sulfur	1.3	8.7	1.4	8.6	2.6	7.4	2.7	7.3	86.7 to 75.3
$BaSO_4$	$Cu_2Fe(CN)_6$	6.2	3.8	6.3	3.7	7.2	2.8	7.3	2.7	81.7 to 74.8
$BaSO_4$	Fe_2O_3	0.5	9.5	0.6	9.4	8.7	1.3	8.8	1.2	99.2 to 54.4
$BaSO_4$	SnO_2	2.1	7.9	2.2	7.8	7.3	2.7	7.4	2.6	89.6 to 47.6

cent of the former. The shaded portions of the diagram thus represents the composition of the coagulum in the range of mutual coagulation in weight per cent of the dry constituents.

The composition of the precipitates using each positive sol with the several negative sols is represented in the order of increasing amounts of the negatively charged constituent, assuming that the midpoint of the range of complete mutual coagulation is the optimum point. It will be noted that the order in which the negative sols arrange themselves is not the same even for the hydrous oxide sols and is quire different with a different type of sol such as barium sulfate.

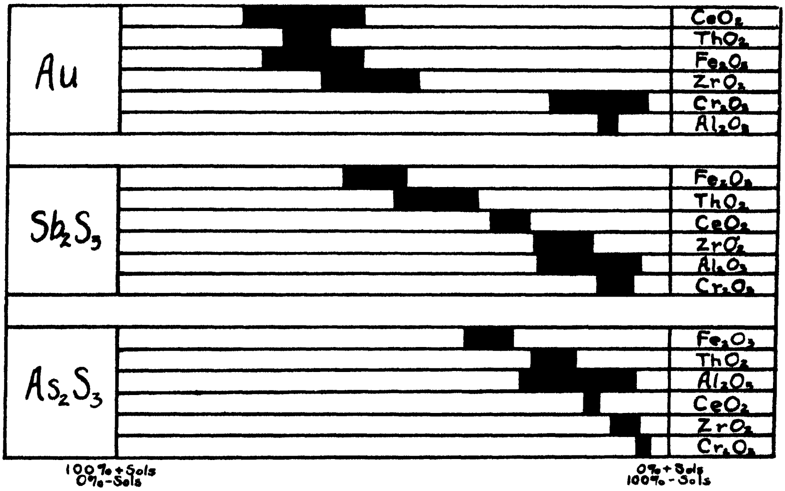

FIG. 3
Range of mutual coagulation of oppositely charged sols (Biltz).

Second Series. The results recorded above were extended in a second series of experiments with different sols. The method of procedure in obtaining the zone of mutual coagulation was the same as that previously described except that the sols were mixed in such amounts that the total volume of the mixture was always 10 cc. The results are recorded in Tables VII to X and are shown in the diagram Fig. 2.

Observations of Biltz. From the mutual coagulation observations of Biltz,[1] the zone of complete mutual coagulation was estimated. These data are shown in Table XI and are plotted in Fig. 3. The hydrous oxides, which give positive sols, are arranged in order of decreasing amount in mixtures with Au, Sb_2S_3 and As_2S_3, respectively, assuming that the optimum point of mutual coagulation is the midpoint of the range. In this series of experiments also it will be seen that the order of oxides is by no means the same, as usually assumed.

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[1] Ber., 37, 1104 (1904).

TABLE XI

Mutual Coagulation Data of Biltz

Milligrams of constituents in coagulam in the zone of mutual coagulation				Range of mutual coagulation Per cent by weight	
Au	1.4	CeO_2	4.8 to 1.8	CeO_2	77.5 to 56.0
Au	1.4	ThO_2	3.2 to 2.3	ThO_2	70.0 to 62.0
Au	1.4	Fe_2O_3	4.0 to 1.8	Fe_2O_3	74.0 to 56.0
Au	1.4	ZrO_2	2.2 to 1.2	ZrO_2	63.0 to 46.0
Au	1.4	Cr_2O_3	0.4 to 0.55	Cr_2O_3	22.0 to 4.0
Au	1.4	Al_2O_3	0.2 to 0.15	Al_2O_3	12.5 to 9.5
Sb_2S_3	5.6	Fe_2O_3	8.0 to 5.2	Fe_2O_3	50.0 to 48.0
Sb_2S_3	28.0	ThO_2	5.5 to 3.0	ThO_2	50.0 to 35.0
Sb_2S_3	28.0	CeO_2	13.5 to 9.6	CeO_2	32.5 to 25.5
Sb_2S_3	28.0	ZrO_2	9.1 to 4.5	ZrO_2	24.5 to 14.0
Sb_2S_3	28.0	Al_2O_3	9.0 to 1.5	Al_2O_3	24.0 to 5.0
Sb_2S_3	28.0	Cr_2O_3	4.0 to 2.0	Cr_2O_3	12.5 to 6.5
As_2S_3	12.0	Fe_2O_3	7.0 to 4.8	Fe_2O_3	37.0 to 28.5
As_2S_3	12.0	ThO_2	3.5 to 2.5	ThO_2	22.5 to 17.0
As_2S_3	24.0	Al_2O_3	9.0 to 1.5	Al_2O_3	27.0 to 6.0
As_2S_3	24.0	CeO_2	4.0 to 3.5	CeO_2	15.0 to 12.5
As_2S_3	24.0	ZrO_2	2.7 to 1.3	ZrO_2	10.0 to 5.0
As_2S_3	12.0	Cr_2O_3	2.7 to 0.4	Cr_2O_3	5.5 to 3.0

Discussion of Results

From the observations summarized in Figs. 1, 2, and 3 of the preceding section, the following facts in connection with the mutual coagulation process are brought out: First, the complete mutual coagulation of two sols of opposite charge may take place over a narrow range of concentrations or over quite a large range of concentrations. Second, when, for example, a given series of positive sols is arranged in order of the optimum concentration for mutual coagulation on mixing with negative sols, the order of the positive sols may vary widely with different negative sols.

These results indicate that the mutual coagulation process may be determined by a number of factors that are effective to different degrees with different sols. The more important of these will be considered in a general way in the following paragraphs.

1. *Mutual Electrical Neutralization.* Since coagulation takes place when the charge on the particles of a sol is reduced to a critical value below which the particles will agglomerate into aggregates sufficiently large to settle, it would seem to follow that, if no other factor comes in, mutual coagulation would result when amounts of sols bearing equal numbers of opposite charges are mixed. Moreover, if electrostatic neutralization were the only factor, one would expect the range of mutual coagulation to be relatively narrow and that

a given series of sols of one sign would always arrange themselves in the same order regardless of what sol of opposite sign is precipitated. From the experimental results it is obvious that the precipitating power of sols of one sign for sols of opposite sign is not determined exclusively by the charge on the colloidal particles. It may be, however, that this is the predominating factor when the range of coagulation is quite narrow.

Mutual Adsorption of Colloidal Particles. Since the mutual coagulation process is not independent of the nature of the colloidal particles, it is altogether probable that a specific adsorption between the two kinds of particles that is not determined by their electrical charge, will have an important effect in determining the range of mutual coagulation. Thus, if the mutual attraction is relatively great between two electrical neutral particles which yield sols of opposite sign, one would expect this force of attraction to supplement the electrostatic attraction between the oppositely charged colloidal particles and thereby extend the range of mutual coagulation. Fifteen years ago Bancroft[1] called attention to the importance of adsorption of the particles of one colloid by those of another in the mutual coagulation process, but his paper has been overlooked or has not been taken seriously by most people. Unfortunately, the magnitude of the effect on the mutual coagulation process, of mutual adsorption of particles which is independent of their charge, cannot be evaluated quantitatively until the magnitude of the mutual adsorption force is known.

Precipitating Ions in the Sols. The effect of the presence of unadsorbed multivalent ions in the sols as a factor in the mutual coagulation process has not been taken into account by anybody. For example, if the excess alkali ferricyanide used in the preparation of a negatively charged ferricyanide sol is not removed completely and this sol is employed to coagulate positive sols the ferricyanide ion in the intermicellar solution will exert a precipitating action on the positive sol that is independent of the mutual coagulation of the oppositely charged particles. In such a case one would expect the range of coagulation to be relatively wide. In arranging the sols of one charge in order of their precipitating action toward sols of opposite charge it is not permissible to take the midpoint of the zone as the optimum mutual coagulation point, if a part of the coagulation is true electrolyte coagulation. In the experiments recorded above an attempt was made to avoid this complication by working with well dialyzed sols.

Interaction between Stabilizing Ions. Attention has been called to the observations of Lottermoser and of Thomas and Johnson, which show that interaction between stabilizing ions with the formation of an insoluble or slightly ionized compound, may sometimes play an important role in the mutual coagulation process. However, even in cases where such an interaction is possible, it is altogether unlikely that the effect is independent of the electrostatic attraction and the specific adsorption between the colloidal particles. Certainly, one gets mutual coagulation where removal of stabilizing ions by chemical neutralization or precipitation is a remote possibility (Table I.)

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[1] J. Phys. Chem., 19, 362 (1915).

In a subsequent paper special attention will be given to the effect on the width of the mutual coagulation zone of (1) mutual adsorption of the colloidal particles and (2) the presence of multivalent precipitating ions as impurities in the sols.

Summary

The results of this investigation are as follows:

1. The zone of complete mutual coagulation of two sols of opposite sign may be very narrow or quite broad.

2. When a given series of positive sols, for example, is arranged in order of the optimum concentration for mutual coagulation on mixing with negative sols, the order of the positive sols may vary widely with different negative sols.

3. The behavior noted in 1 and 2 is accounted for by the fact that the precipitating power of positive sols for negative sols is not determined exclusively by the charge on the colloidal particles. Other facts which influence the mutual coagulation process are (1) mutual adsorption of colloidal particles, that is independent of their charge (2) the presence of precipitating ions as impurities in the sols and (3) interaction between stabilizing ions.

4. Complete mutual coagulation is not due in general to interaction and consequent removal of the stabilizing electrolytes of oppositely charged sols; but this factor may be important in certain cases.

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A STUDY OF COLLOIDAL FERRIC OXIDE AND VARIOUS FACTORS WHICH INFLUENCE ITS ABILITY TO CATALYZE THE DECOMPOSITION OF HYDROGEN PEROXIDE*

I. The Temperature Coefficient, the Effect of Catalyst Concentration and the Effect of Electrolytes

BY RAYMOND J. KEPFER AND JAMES H. WALTON

Introduction

In spite of the fact that numerous investigations have been made on the decomposition of H_2O_2 by various colloidal systems only a few are mentioned in the literature concerning the decomposition of this substance by colloidal ferric oxide. The first of these was reported by Duclaux[1] in brief in 1907 and then in more detail in 1923. He found the reaction to be monomolecular with the velocity constants for any one reaction varying by as much as 10%. He also stated that the catalytic activity of the sol was determined by the amount of Fe_2Cl_6 in the colloidal particle and not by the amount of iron oxide. The addition of either K_2SO_4 or $K_4Fe(CN)_6$ inhibited the reaction. This inhibition he attributed to a true chemical reaction; for example

$$Fe_2Cl_6.nFe_2O_3 + 3\ K_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 6\ KCl + nFe_2O_3.$$

He stated further that the sulphate had less effect than the ferrocyanide because the former gives a soluble product and thus an incomplete reaction while the latter forms an insoluble product and thus a complete reaction. More will be said concerning this work of Duclaux when the authors introduce some contradictory evidence. Shpitalskii, Petin and Burova[2] have also made an investigation in which they added various amounts of HCl or NaOH to dilute solutions of $Fe_2(SO_4)_3$ or $FeCl_3$ and then studied the effect of these hydrolyzing mixtures on the decomposition of H_2O_2.

Purpose

By means of a special high-temperature dialyzer Sorum[3] has succeeded in preparing a so-called "chloride-free" ferric oxide sol. Due to the fact that previous investigations of the decomposition of H_2O_2 by colloidal ferric oxide have been few in number, not so very extensive, and have made use of ferric oxide sols containing much more electrolyte than that prepared by Sorum, a more extensive investigation of this decomposition using a sol prepared by the method developed by Sorum is desirable.

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*Contribution from the Laboratory of General Chemistry of the University of Wisconsin. This communication is an abstract of a part of a thesis submitted to the Graduate School in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[1] Duclaux: Compt. rend., **145**, 802 (1907); J. Chim. phys., **20**, 18 (1923).

[2] Shpitalskii, Petin and Burova: J. Russ. Phys. Chem. Soc., **60**, 1271, 1291, 1317 (1928).

[3] Sorum: J. Am. Chem. Soc., **50**, 1263 (1928).

Experimental

Preparation of the Reagents.

The H_2O_2 used for this investigation was obtained by distilling Merck's 30% Superoxol in a Pyrex apparatus under reduced pressure and was stored in a quartz flask in the dark. The iron oxide sol was prepared by dropping a molar solution of $FeCl_3$ into vigorously boiling water in a Pyrex flask which had previously been steamed. The sol was dialyzed using the dialyzer and method developed by Sorum at a temperature of 85°-90° for three days after which it gave no test for chloride ion using $AgNO_3$. After dialysis the sol was stored in a large Pyrex flask which had likewise been previously steamed. Throughout the course of the investigation great care was taken to keep these stock reagents tightly stoppered as much of the time as possible. The iron oxide sol was withdrawn from the stock solution about 500 cc. at a time and stored in a small flask so as to open the stock solution container as seldom as possible. Each of these 500 cc. portions was titrated for iron content using the method reported by Knop.[1] Steamed Pyrex was used throughout the investigation since Ayres[2] found that iron oxide sols soon dissolved enough impurities from soft glass to change considerably such properties as flocculation values, etc.

Clayton,[3] Walton and Judd,[4] and likewise Lottermoser and Lehmann[5] have shown that in a decomposition of H_2O_2 the impurities in the water used are of utmost importance. For this reason all water used in this investigation for dilution purposes, making up solutions and the like was prepared in a conductivity-water still and kept in the usual manner.

The speed of the reaction was followed by titrating the undecomposed H_2O_2 with $KMnO_4$ in the presence of H_2SO_4. To make sure that colloidal iron oxide in the amounts used would not interfere with this titration, equal samples of H_2O_2 were withdrawn from a stock solution and titrated, some in the presence of colloidal iron oxide and some in its absence. It was found that checks could be obtained quite easily when the aqueous solution of H_2SO_4 used for rinsing out and diluting the samples contained enough $KMnO_4$ to give it a distinct violet color before using.

Experimental Detail.

After a series of preliminary experiments the following was adopted as a satisfactory method of experimentation. 20 to 25 cc. portions of reaction solution were made up in a 50 cc. beaker as follows. The required volume of conductivity water was run in from a 50 cc. burette. Then the electrolyte solutions, if any were used, were added from 1, 2,5, or 10 cc. pipettes. Next the H_2O_2 was introduced by means of a 2 cc. pipette and finally the iron oxide sol in a similar manner. This order was followed throughout, since Lottermoser and Lehmann have shown that the order of addition of the constituents of the solution is an important factor.

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[1] Knop: J. Am. Chem. Soc., **46**, 263 (1924).

[2] Ayres: Ph.D. Thesis. Univ. of Wisconsin (1930).

[3] Clayton: Trans. Faraday Soc., **11**, 164 (1915).

[4] Walton and Judd: Orig. Com. 8th. Intern. Congr. Appli. Chem. Appendix, **26**, 621 (1912).

[5] Lottermoser and Lehmann: Kolloid-Z., **29**, 250 (1921).

This solution was then transferred to a 25 cc. burette and quickly run out into ordinary 5 inch Pyrex test tubes, 2 cc. into each test tube. These test tubes were covered with tin foil and black paint so as to exclude all light. The tubes were then corked and placed in a thermostat at 50°. At various intervals the content of one of these tubes of reaction solution was titrated with $KMnO_4$ to determine the amount of undecomposed H_2O_2. The first four runs made in this manner gave times of half life of 74, 77, 73 and 68 minutes which are satisfactory checks.

The following are some factors which affect the actual magnitude of the experimental results. The 2 cc. portions of reaction solution were measured so quickly that they probably lacked a small amount of being 2 cc. Also in spite of the fact that the tubes were corked there was some evaporation. Furthermore, H_2O_2 undergoes some decomposition at 50° when in contact with glass. However all of these sources of actual error are constant so their influence on the relative results of the following investigations can be neglected. Stark[1] has shown that ferric oxide sols are coagulated by oxygen bubbles. However a calculation made using his results and the amount of oxygen given off during one of the decompositions showed that since only about 0.065% of the sol would be coagulated during a run this effect could also be neglected.

However at times some factor did enter which caused considerable error. Although a majority of the runs could be checked within 5%, at times some run would fail to check a duplicate by as much as 30%. This, the writers feel, was due chiefly to the condition of the atmosphere in the room at the time the reaction solution was prepared. This belief is substantiated by the fact that if duplicate solutions were prepared at the same time much better checks could be obtained than when they were prepared at different times. Another reason for this belief is that, if there were enough fumes to give a distinct odor in the room at the time of preparation of a reaction solution, that run would invariably fail to check a run made at another time when no noticeable fumes were present. For this reason duplicate solutions were never prepared at the same time. Of course this would tend to give poorer checks than if the duplicate solutions were prepared at the same time but for a series of determinations from which one wishes to make comparisons more significant values can be obtained by preparing the reaction solutions at different times.

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[1] Stark: J. Am. Chem. Soc., 52, 2730 (1930).

In the experiments that are to follow at least two determinations were made in each case. In all cases the tables give an average of the determinations made under similar conditions.

Method of calculating Results.

It was found that when these results were substituted in the equation for a monomolecular reaction and velocity constants calculated, exact constants were not obtained. This is shown by Table I which gives the average results of four similar runs taken at random from the experiments performed.

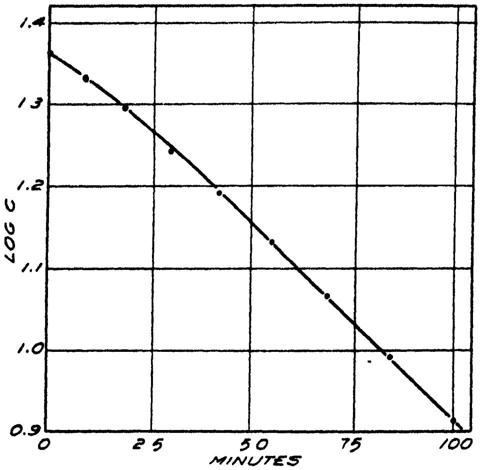

FIG. 1
H_2O_2 Decomposition catalyzed by Iron Oxide Sol.

TABLE I

Velocity Constants calculated for a Monomolecular Reaction
Temperature 50°
Concentration—1.166 grams Fe/l

Min.	cc. $KMnO_4$	Log C.	Log Diff.	k
0	23.08	1.3632	—	—
9	21.48	1.3320	0.0312	0.0080
19	19.72	1.2949	0.0371	0.0085
30	17.47	1.2423	0.0526	0.0110
42	15.56	1.1920	0.0503	0.0097
55	13.57	1.1326	0.0594	0.0105
69	11.55	1.0663	0.0663	0.0109
84	9.48	0.9930	0.0733	0.0113
100	8.21	0.91430.0787		0.0113

Although these constants certainly leave something to be desired in agreement they are as good as others that are reported in the literature for experiments of a similar nature.[1]

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[1] Bredig and Collaborators: Z. physik. Chem., **31**, 258 (1899); **37**, 323 (1901); **37**, 3 (1901); Tartar and Schaffer: J. Am. Chem. Soc., **50**, 2604 (1928); Shpitalskii, Petin and Burova: J. Russ. Phys. Chem. Soc., **60**, 1271, 1291, 1317 (1928).

The average k's were not calculated for most of the comparisons, but instead the average results of duplicate determinations were plotted, log of cc. of $KMnO_4$ against time in minutes, and then the time of half life was obtained from this curve. Such a curve is given for the data of Table I in Fig. 1.

Effect of Temperature.

For this study determinations were made at temperatures of 30°, 40°, 50° and 60°, other conditions being constant. Enough iron oxide sol was used to give a concentration of iron of 1.166 g. per liter. A summary of these results is given in Table II.

TABLE II

Summary of Effect of Temperature on the Reaction

Tem. A°	Min. of 1/2 life	Tem. Coef.	Recip. of Tem.	Log. of 1/2 life	k from 1/2 life	Critical Increment
303°	401	—	0.003300	2.603	0.00173	—
313°	157	2.14	0.003195	2.196	0.00442	17620 cal.
323°	69	2.27	0.003096	1.839	0.01006	16470 "
333°	32	2.58	0.003003	1.505	0.02170	16380 "

The average value of the temperature coefficient was about 2.33. In general when applied to heterogeneous reactions low temperature coefficients, for example 1.3, are associated with reactions in which diffusion is the determining factor while higher temperature coefficients are associated with true chemical reactions. Thus this average temperature coefficient of 2.33 seems to indicate that the decomposition of H_2O_2 is a true chemical reaction and is not dependent upon a process of diffusion so far as velocity is concerned.

However Taylor[1] points out that even though there are many contact catalytic reactions which give temperature coefficients of 1.3 there are many other examples especially with colloidal and enzyme catalysts which give the usual value of 2 or above. This may be due to the fact that the Brownian movement of the colloidal particles eliminates the necessity for diffusion as a determining factor, or it may be due to some surface phenomenon as proposed by Denham.[2] More will be said as to a possible mechanism later.

It has been shown that the relationship between temperature and rate of reaction can be expressed by the familiar equation proposed by van't Hoff and verified by Arrhenius: namely

$$\frac{d \ln k}{dt} = \frac{E}{RT^2}$$

in which k is the velocity constant, R the gas constant, T the absolute temperature and E the critical increment. That the data obtained for the effect of temperature on the reaction are in conformity with this equation is shown by the fact that a straight line (Fig. 2) is obtained when the reciprocals of the absolute temperature (column 4 of Table II) are plotted against the logarithm of the time of half life (column 5 of Table II).

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[1] Taylor: "Treatise on Physical Chemistry", **2**, 954 (1924).

[2] Denham: Z. physik. Chem., **72**, 641 (1910).

If the Arrhenius equation is integrated between two temperatures it takes the form

$$\log \frac{k_2}{k_1} = \frac{E(T_2 - T_1)}{2.303\ R\ T_2\ T_1}.$$

If this equation is used, taking R as 1.98, T_2 and T_1 as the two absolute temperatures, k_2 and k_1 as the corresponding velocity constants then E can be obtained. The k's (given in column 6 of Table II) to be used were obtained by substituting the times of half life (given in column 2 of Table II) into the equation for the velocity constant of a monomolecular reaction. When all these substitutions were made into the integrated equation the values given in column 7 of Table II, the average of which is 16820 calories per gram molecule, were obtained for the critical increment.

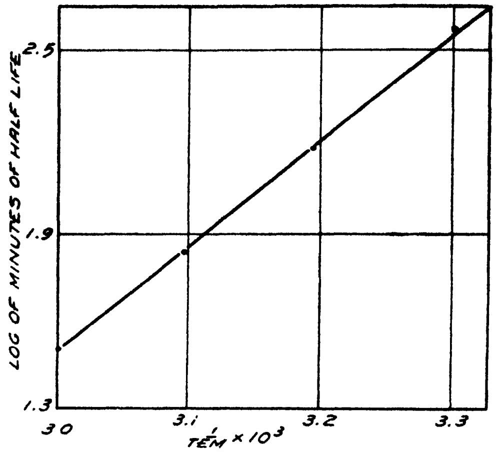

Fig. 2
Effect of Temperature on the Reaction.

Effect of Catalyst Concentration.

In order to study the effect of catalyst concentration on the reaction several determinations, the results of which are given in Table III, were made using various concentrations of the colloidal iron oxide. Runs were

Table III

Summary of Effect of Catalyst Concentration on the Reaction

Temperature 50°C

Grams of Fe/l	Min. of half life	Recip. of half life
0.286	442	0.00226
0.563	168	0.00595
1.166	69	0.01449
1.708	45	0.02222
2.281	35	0.02857

not attempted at concentrations above 2.281 g. of iron per liter because at this concentration the iron oxide sol gave so much color to the solutions to be titrated that $KMnO_4$ end points were difficult to determine. As is shown by Fig. 3 a straight line is obtained when the reciprocal of the time of half life (given in column 3 of Table III) is plotted against the concentration of the catalyst, hence the speed of reaction is directly proportional to the amount of catalyst present between the limits used.

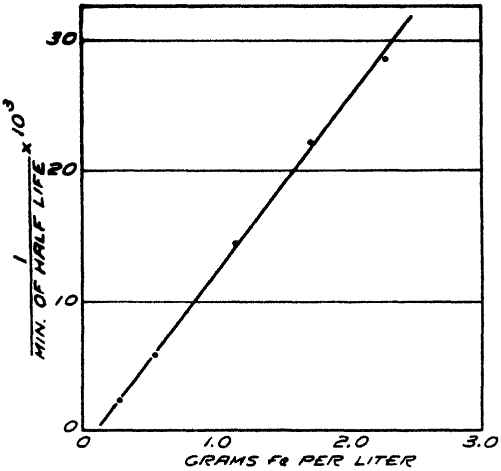

FIG. 3
Effect of Catalyst Concentration on the Reaction.

If now we read from this curve the reciprocal of the time of half life at concentrations of 0.5, 1, and 2 g. of iron per liter and divide one into another in turn we get 2.3 and 2.1 the average being 2.2. Hence on an average doubling the concentration of the colloidal catalyst multiplies the speed of reaction by 2.2. This is slightly lower but of the same order as other values given for reactions of a similar nature.[1]

Effect of Added Electrolytes

A great deal of work has been done on the effects of preservatives, inhibitors, negative catalysts or poisons upon the decomposition of H_2O_2 by colloids. As examples the investigations of Brossa,[2] Bredig and his collaborators, Loevenhart and Kastle,[3] Meyerhof,[4] Tartar and Schaffer, Iredale,[5] and Maxted[6] may be cited. Various reasons may be given for this inhibition. Electrolytes in general are probably adsorbed on the colloid, thus reducing the amount of exposed surface while some substances may exert a stabilizing influence on the H_2O_2.

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[1] Bredig and von Berneck: Z. physik. Chem., **31**, 258 (1899); Bredig and Reinders: **37**, 323 (1901).

[2] Brossa: Z. physik. Chem., **66**, 162 (1909).

[3] Loevenhart and Kastle: Am. Chem. J., **29**, 397 (1903).

[4] Meyerhof: Arch. ges. Physiol., **157**, 351 (1914).

[5] Iredale: J. Chem. Soc., **119**, 109 (1921).

[6] Maxted: J. Chem. Soc., **121**, 1760 (1922).

In spite of all this work on inhibition of catalytic reactions, little has been done with any inhibitors where catalysis of H_2O_2 decomposition by colloidal iron oxide is involved. Shpitalskii, Petin and Burova have studied the effects of NaOH and HCl on solutions of $FeCl_3$ and $Fe_2(SO_4)_3$ which were undergoing hydrolysis and at the same time catalyzing the decomposition of H_2O_2. As mentioned before Duclaux found that only very small additions of K_2SO_4 or $K_4Fe(CN)_6$ were necessary to double or even triple the time of half life of an H_2O_2 decomposition by his colloidal iron oxide catalyst.

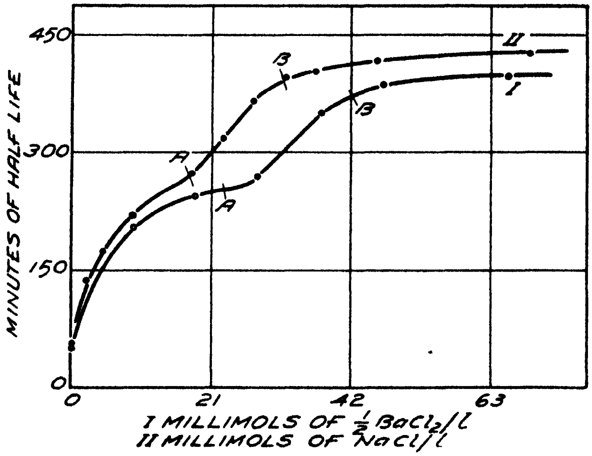

FIG. 4
Effect of NaCl and $BaCl_2$ on the Reaction.

Effect of NaCl.

In each case 21.66 cc. of reacting solution were prepared. Each of these solutions contained 0.465 g. of iron per liter and NaCl in amounts up to 68.85 millimols per liter. The results are given in Table IV and in Fig. 4, Curve II.

The curve so obtained might be divided into four parts; namely, (1) the first portion in which an addition of a small amount of salt causes a great decrease in the catalytic activity of the sol; (2) a gradual changing so that

TABLE IV
Summary of Effect of NaCl on the Reaction
Temperature 50°
0.465 g. Fe/l

Millimols NaCl/l	Min. of half life	Millimols NaCl/l	Min. of half life
0	56	27.54	364
2.30	136	32.13	397
4.59	173	36.72	403
9.18	221	45.90	415
18.36	270	68.85	426
22.95	317		

further additions of NaCl do not make so much difference in the catalytic activity of the sol; (3) another portion where small additions of NaCl greatly decrease the rate of reaction; (4) and finally a portion where the speed of decomposition is only slightly affected by addition of more NaCl.

The first two divisions are very similar in form to the adsorption isotherms first proposed and studied by Freundlich.[1] Since the colloidal iron oxide is acting as the catalyst for the H_2O_2 it must obviously be necessary for the molecules of H_2O_2 to come into contact with the particles of colloid for decomposition to take place. Then any change which takes place which would prevent the H_2O_2 molecules from coming into contact with the colloidal particles will slow down the reaction velocity. Accordingly, the conclusion that one may draw from these first two parts of curve II in Fig. 4 is that the rate of reaction is being slowed down by the adsorption of chloride ions on the particles of colloidal iron oxide catalyst. Thus the first two parts of this curve not only look similar to an adsorption curve but seemingly they correspond to one or may even be considered as being one. Evidently this method of studying the decomposition of H_2O_2 by colloidal iron oxide in the presence of various amounts of NaCl might be adapted to the study of the relative adsorption of chloride ions by colloidal iron oxide.

Although the change from the second to third portion of the curve is not an abrupt break, it is sudden enough to show that some distinct change has taken place. The same can also be said of the transition from the third to the fourth part of the curve. Bancroft[2] has pointed out that coagulation is always preceded by adsorption, hence if we attribute the first parts of the curve to adsorption effects then the next thing to expect would be flocculation of the sol and its effects on the reaction velocity. In order to reach some conclusion concerning this possibility, an investigation of the flocculation of the sol by NaCl in the presence of H_2O_2 was undertaken. For this study conditions throughout were maintained as nearly identical as possible with the conditions under which the decomposition studies were made. At the end of four hours observations were made as to the degree of flocculation.

On the basis of these flocculation studies two cross-marks A and B have been placed on the curve under discussion. A corresponds to the point at which the first signs of turbidity were observed, and B to the point at which complete precipitation took place. The third division (i.e. A B) of this curve then corresponds to the region of flocculation of the iron oxide sol. During this period the colloidal particles of iron oxide are probably uniting to form much larger particles, thus causing a great decrease in its specific surface. Such an action would doubtless slow down the decomposition velocity. Since the limits of this third part of the curve correspond to the limits of flocculation of the sol, this procedure might be employed to determine the flocculation value of an iron oxide sol by NaCl in the presence of H_2O_2. To be sure it would be a slow method to employ for such a purpose, but evidently it will give results both for the point at which flocculation starts to take place and for the point at which it is complete.

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[1] Freundlich: Z. physik. Chem., **44**, 129 (1903); **57**, 385 (1907).

[2] Bancroft: "Applied Colloid Chemistry" (1926).

After all of the iron oxide has been coagulated, further additions of NaCl can cause only slight changes in the physical make up of the coagulated oxide. However, Weiser[1] has shown that even the coagulated ferric oxide adsorbs more electrolyte. As before, this adsorption will cover up still more of the catalyst surface and thus further retard the rate of decomposition of the H_2O_2. The fourth part of the curve (i.e. from B to the right) in which further additions of NaCl cause only a slight decrease in the decomposition rate of H_2O_2, then is quite likely due to a further adsorption of NaCl by the coagulated ferric oxide.

Effect of $BaCl_2$.

$BaCl_2$ was chosen as the next substance to be used as a flocculating electrolyte. Since this electrolyte contains the same negative ion as NaCl this series of determinations should serve chiefly as a check on the preceding curve. For each run 21.44 cc. portions of reaction solution were prepared. This solution contained 0.465 g. of iron per liter, $BaCl_2$ in amounts up to 65.36 millimols of 1/2 $BaCl_2$ per liter and 2.53 cc. of stock solution of H_2O_2. The results are given in Table V.

These results were plotted in the same manner as before and curve I in Fig. 4 thus obtained. A flocculation value study was also made using $BaCl_2$ as the coagulating electrolyte. In the same manner as before the points corresponding to first signs of turbidity and complete flocculation are indicated by cross lines A and B on curve I Fig. 4. As is quite evident this curve is very similar to that obtained when NaCl was employed as the flocculating agent. The writers have chosen to call these curves "flocculation curves" since they are so similar in form to those obtained in ordinary potentiometric titrations of acids against bases or of oxidizing agents against reducing agents. In somewhat the same manner as these latter curves show when neutralization or oxidation and reduction are complete so these flocculation curves show when flocculation is complete.

TABLE V

Summary of the Effect of $BaCl_2$ on the Reaction

Temperature 50°

0.465 g. Fe/l

Millimols 1/2 $BaCl_2$/l	Minutes of half life	Millimols 1/2 $BaCl_2$/l	Minutes of half life
0	51	37.35	350
9.34	205	46.69	384
18.67	244	65.36	396
28.01	265		

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[1] Weiser: J. Phys. Chem., 25, 399 (1921).

Effect of K_2SO_4.

A flocculating ion having a valence of two was next used, K_2SO_4 being chosen as a representative electrolyte. 21.44 cc. portions of reaction solution were prepared. Each of these contained 0.465 g. of iron per liter, K_2SO_4 in amounts up to 0.560 millimol per liter and 2.47 cc. of stock H_2O_2 solution. A summary of the results is given in Table VI. The data contained in this table have been plotted in Fig. 5, curve II. The limits of the realm of flocculation are indicated by A and B. The curve so obtained is of the same general form as were the curves when NaCl and $BaCl_2$ were used.

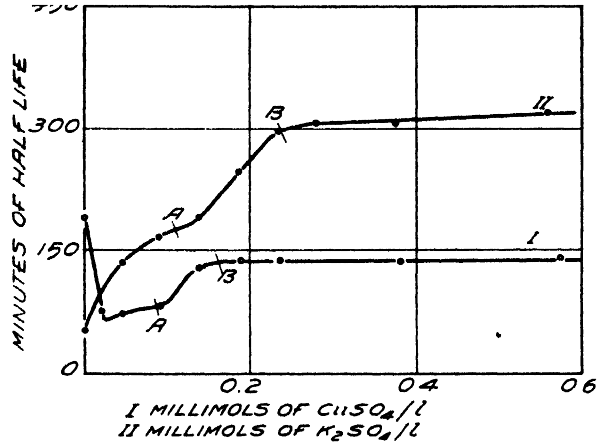

Fig. 5
Effect of K_2SO_4 and $CuSO_4$ on the Reaction.

TABLE VI
Summary of Effect of K_2SO_4 on the Reaction
Temperature 50°
0.465 g. Fe/l

Millimols K_2SO_4/l	Minutes of Half life	Millimols K_2SO_4/l	Minutes of Half life
0	51	0.233	296
0.047	139	0.280	306
0.093	164	0.373	306
0.140	191	0.560	320
0.187	246		

Effect of Na_2HPO_4.

Having studied the effects of a monovalent and a divalent ion on this decomposition the next logical substance to use would be a trivalent ion. Since acids and bases have a decided effect upon the stability of H_2O_2, it was desired to use some salt which would be as nearly neutral as possible. Na_2HPO_4, which is only slightly basic to phenolphthalein, was chosen as the electrolyte to be studied. The results are given in Table VII. The data contained in this latter table have been plotted and curve I of Fig. 6 thus obtained. The limits of flocculation are indicated by cross lines A and B on the curve.

This curve is somewhat different from the others already mentioned. At the beginning where the other curves gave two parts which corresponded to an adsorption isotherm, in this curve these two parts have flattened down into one part, that is, the first additions of phosphate ion do not have the relatively large effect of later additions of more phopsphate ion as was noticed in the case of the other flocculating ions. Secondly the break in the curve when flocculation begins is rather indefinite. Thirdly, there is no ap-

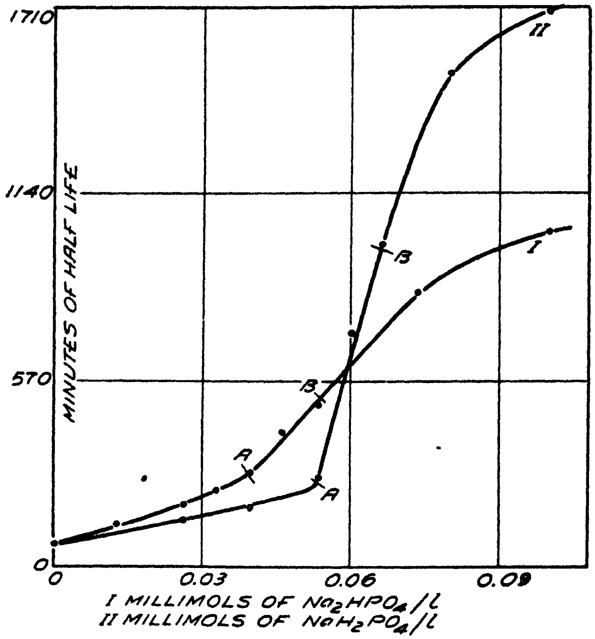

Fig. 6
Effect of Na_2HPO_4 and NaH_2PO_4 on the Reaction.

Table VII

Summary of Effect of Na_2HPO_4 on the Reaction
Temperature 50°
0.465 g. Fe/l

Millimols Na_2HPO_4/l	Minutes of half life	Millimols Na_2HPO_4/l	Minutes of half life
0	66	0.0467	409
0.0133	124	0.0534	495
0.0267	190	0.0734	832
0.0333	234	0.1000	1020
0.0400	291		

parent break in the curve at the point which corresponds to complete flocculation, and fourthly, after flocculation has taken place the rate of decomposition is much less than in the cases previously cited.

A majority of these differences can be explained by the stabilizing influence[1] of the phosphate ion on H_2O_2. For example, ortho phosphoric acid, although it is a weak acid, is a fairly good preservative for solutions of H_2O_2 and Quiesser[2] mentions the use of a mixture of salicylic acid and Na_2HPO_4 as a preservative for H_2O_2. Furthermore, Menzel and Gäbler[3] found that both Na_2HPO_4 and NaH_2PO_4 form addition compounds with H_2O_2 which are quite stable. This would account for the fact that the decomposition is greatly reduced after the iron oxide had been completely coagulated. The lack of a break in the curve at the point of complete flocculation would thus be accounted for, since no sudden change would take place if the addition of phosphate ion continues to decrease the rate of decomposition of the H_2O_2 after coagulation of the sol. The lack of a sudden break in the curve at the point which corresponds to the beginning of flocculation can be attributed at least in part to a similar cause. If one takes into account the fact that only very small concentrations of phosphate ion are required to have nearly a maximum stabilizing influence, it may be supposed that the slight break in the curve that finally does occur is due to the fact that the phosphate ion concentration is nearing the point where maximum stabilizing influence is reached.

There still remains an explanation of why the lower portion of the curve comes so close to being a straight line instead of taking the form of an ordinary adsorption isotherm. Several factors may exert some influence, among these being the following: the adsorption of phosphate ion by colloidal ferric oxide, the stabilizing effect of the phosphate ion on H_2O_2, and the effect of the slight basicity of the Na_2HPO_4. No one of these in itself seems sufficient to explain the course of the first part of the curve and just what the combined effect of all these together with other possible factors would be is difficult to foretell.

Effect of NaH_2PO_4.

As a check on the results obtained with Na_2HPO_4 similar studies were made with NaH_2PO_4. A summary of the results of these determinations is given in Table VIII. The data given in this table have been plotted to give curve II of Fig. 6. The limits of flocculation have been indicated on the curve in the usual manner.

As is evident from Fig. 6 the two curves are very similar. The following differences may be mentioned. In this second curve the point at which flocculation begins is indicated by a distinct break in the curve. It will also be noticed that the larger concentrations of NaH_2PO_4 slow down the reaction rate more than do equivalent concentrations of Na_2HPO_4. This can easily

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[1] Fischer: Pharm. Zentr., **48,** 57 (1907); Dohme and Engelhardt: Am. J. Pharm., **82,** 69 (1910); Jensen: Chem. Drug., **93,** 1036 (1920).

[2] Queisser: Ger. Pat., **321, 616,** April 20 (1919).

[3] Menzel and Gäbler: Z. anorg. allgem. Chem., **177,** 187 (1928).

TABLE VIII

Summary of Effect of NaH_2PO_4 on the Reaction

Temperature 50°

0.465 g. Fe/l

Millimols NaH_2PO_4/l	Minutes of half life	Millimols NaH_2PO_4/l	Minutes of half life
0	66	0.0600	715
0.0267	142	0.0667	980
0.0400	181	0.0800	1500
0.0534	272	0.1000	1700

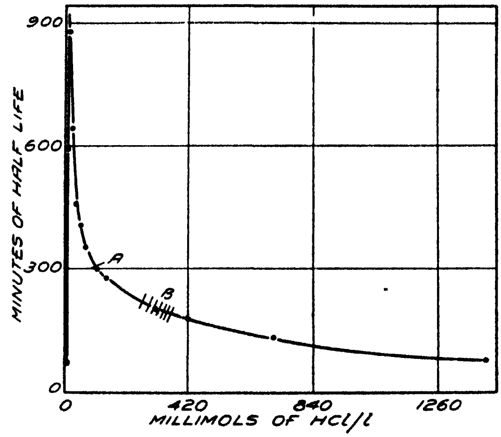

FIG. 7
Effect of HCl on the Reaction.

be accounted for when we recall that H_2O_2 is more stable in an acid solution than it is in a basic one. Freundlich found that the amounts of mono, di, and trivalent ions necessary to cause coagulation of a sol are in the ratio of about 500 to 7 to 1. Although the determinations in the present investigations were made in the presence of H_2O_2 the corresponding ratio was found to be of about the same order but of a somewhat different magnitude. Roughly the flocculation values obtained in this investigation using chloride, sulphate, and phosphate ions were in the ratio of 700 to 4 to 1.

Effect of HCl.

The effect of HCl was investigated next since it offered interesting possibilities. It is formed when the colloidal ferric oxide is prepared and there are some doubts as to whether or not it can be entirely removed by the process of dialysis. The results are given in Table IX. The data in this table are plotted in Fig. 7. On the basis of flocculation studies a cross line A has been placed on the curve to indicate the first appearance of turbidity and a series of broken lines B to indicate as nearly as possible the realm of complete precipitation. In this study, as was the case with Freundlich's work, no definite flocculation value could be obtained.

TABLE IX

Summary of Effect of HCl on the Reaction.

Temperature 50°.

0.496 g. Fe/l.

Millimols HCl/l	Minutes of half life	Millimols HCl/l	Minutes of half life
0	73	106.2	298
2.9	592	141.7	274
8.7	880	302.9	202
17.4	640	705	133
35.4	455	1420	78
52.8	400	2125	52
70.8	350	4250	15.5

The curve for the results of these determinations is decidedly different in form than any of the others thus far obtained. The activity of the catalyst is greatly decreased by the first additions of HCl due, perhaps, to the high adsorbability of the hydrogen ions. To this must also be added the adsorption of the chloride ions and also the fact that an acid stabilizes a solution of H_2O_2.

The rest of the curve can be explained in the following manner. Let it be assumed that after a small amount of HCl has been added it begins dissolving some of the iron oxide particles. This would give ferric ions which are fairly strong catalysts for the decomposition of H_2O_2, so that at that concentration of HCl at which enough ferric ions are formed to overcome the effects of further adsorption the reaction velocity will begin to increase as more HCl is added. From the curve it seems likely that at 50° this point is at a concentration of about 9 millimols of HCl per liter. As is shown by the curve further additions of HCl continue to increase the rate of decomposition at first rather rapidly, and then as there is less undissolved iron oxide remaining the rate of acceleration gradually decreases until finally further additions of HCl increase the speed of decomposition by only a very small amount. Since in the last determinations the iron oxide was all dissolved, the slight increase in speed of the decomposition is quite likely due chiefly to the rapidity with which the oxide dissolves and not to the amounts of it dissolved at the end of the run. As is further evidenced by the curve the catalytic effect of the ferric ions formed by the dissolving of the ferric oxide by the HCl is so great in proportion to the effect of the undissolved iron oxide, either colloidal or coagulated, that the curve extends right through the complete realm of flocculation without giving any indication that such an act has taken place.

Effect of NaOH.

The effect of sodium hydroxide was next investigated. A summary of these results is given in Table X. The significant results of the corresponding flocculation studies are given along with the curves in Fig. 8.

Curve I is for the addition of relatively small amounts of NaOH and has been plotted on a large scale (indicated at the bottom of Fig. 8). Curve II is for the whole series of determinations and is necessarily plotted on a much smaller scale (indicated at top of Fig. 8). The latter curve is still more complicated than any of the previous ones. An unusual curve was expected due to the

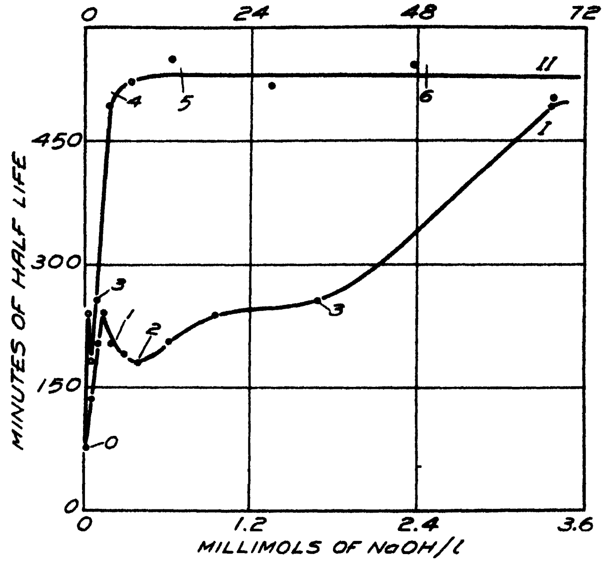

FIG. 8

Effect of NaOH on the Reaction
0-1. Stable positive sol.
1-2. Realm of precipitation of positive sol.
2-3. Complete precipitation of positive sol.
3-4. Restabilization of the sol.
4-5. Realm of stable negative sol.
5-6. Realm of precipitation of negative sol.
6- . Complete precipitation of negative sol.

TABLE X

Summary of Effect of NaOH on the Reaction.
Temperature 50°.
0.496 g. Fe/l.

Millimols NaOH/l	Minutes of half life	Millimols NaHO/l	Minutes of half life
0	73	0.933	239
0.015	90	1.675	256
0.046	134	3.35	490
0.093	205	6.70	515
0.139	241	12.14	546
0.186	205	26.81	514
0.279	194	47.12	540
0.372	183	67.15	500
0.597	210		

several factors that enter into the reaction. Among these are the following: (1) the increased rate of decomposition of H_2O_2 in the presence of a base, (2) the high adsorbability of the OH ion, (3) the fact that NaOH not only flocculates a positively charged ferric oxide sol, but in larger amounts causes the formation of a stable negatively charged sol, and, finally, in larger amounts causes the precipitation of this negatively charged sol.

As with most of the other curves the adsorption of the first amounts of electrolyte greatly decreases the activity of the catalyst. In most of the preceding examples the effects of adsorption became much less as more electrolyte was added. Such is probably the case here but when this happens the ability of NaOH to accelerate the decomposition of the H_2O_2 has a chance to make itself apparent, so that over a short range the rate of decomposition of H_2O_2 is increased by additions of NaOH. This continues until the sol has been precipitated and NaOH has been added in amounts up to where further additions do not have so much effect on the decomposition of H_2O_2. Then (point 2 on the curve) adsorption effects predominate again, and the ferric oxide continues to become less active as more NaOH is added. This evidently continues until the iron oxide has finally adsorbed all the NaOH that it can, and then (to the right of point 4 on the curve) the rate of decomposition of the H_2O_2 is not appreciably changed by further additions of NaOH. The surprising part of it is, that all of this latter change after the precipitation of the positively charged sol seems to be independent of the state of stability of the sol. If it is assumed that exposed surface is the chief deciding factor, then the amount of freely exposed surface of the iron oxide after first precipitation must depend almost entirely upon the amount of adsorbed NaOH and very little, if any at all, on the state of the iron oxide, that is, whether it is present as a precipitated positively charged sol, a stable negatively charged sol, or a precipitated negatively charged sol.

Effect of $CuSO_4$.

In their study of the decomposition of H_2O_2 by ferric salts Bohnson and Robertson[1] found that cupric ions acted as promoters. These contributions of Bohnson and Robertson suggested that a cupric salt be studied. The results of such a study are given in Table XI.

If Curve I Fig. 5 is divided into four parts as was done with the first curves in this investigation it will be noted that all the parts are very similar to the K_2SO_4 curve, except the first section. This first part of the curve is apparently due to the promoter effect studied by Bohnson and Robertson. Evidently this promoter effect of very small amounts of cupric ions is greater than the adsorption effects of small amounts of sulphate ion, so that the activity of the catalyst is increased by additions of very small amounts of cupric ion.

[1] Bohnson and Robertson: J. Am. Chem. Soc., **45**, 2512 (1923); Robertson: **47**, 1299 (1925).

TABLE XI

Summary of Effect of $CuSO_4$ on the Reaction

Temperature 50°.

0.227 g. Fe/l.

Millimols $CuSO_4$/l	Minutes of half life	Millimols $CuSO_4$/l	Minutes of half life
0	191	0.1907	136
0.0234	75	0.238	135
0.0469	73	0.381	133
0.0937	82	0.572	139
0.1406	129		

A flocculation curve has been plotted in Fig. 5 Curve I, and the results of the flocculation studies indicated as before. In this case two hours was chosen as the time of observation for that was more nearly the average time of half life of the various runs.

Mechanism of the Reaction

Earlier in this discussion reference was made to an investigation by Duclaux of the decomposition of H_2O_2 by colloidal ferric oxide. In this study Duclaux reached the conclusion that only the ferric ions which had not been removed from the colloidal iron oxide by dialysis acted as a catalyst and that the effects of various poisons on this reaction could be explained by their chemical reaction with these ferric ions. Bredig and von Berneck have also found evidence to indicate that colloidal ferric hydroxide has almost no effect on the decomposition of H_2O_2. Shpitalskii, Petin and Burova have stated that in an acid medium the ferric ions act as the catalyst while in an alkaline solution the actual catalyst is hydrated particles of Fe_2O_3. Spring[1] is also of the opinion that some of the catalytic effect is due to the colloidal particles in the solution.

From the results obtained in the present investigation the authors feel that almost beyond all doubt the colloidal iron oxide does act as the catalyst for the decomposition of H_2O_2. Practically all the data herein point towards that fact. The first portions of the flocculation curves obtained by the use of NaCl, $BaCl_2$, and K_2SO_4 are so similar in form to ordinary adsorption isotherms, that the most logical explanation is that these salts in being adsorbed by the colloid cover up some of its surface so that it can no longer act as a catalyst. Furthermore, the second part of the curve obtained by the use of $CuSO_4$ seems to correspond to the latter part of an adsorption isotherm. And moreover, the exceedingly large effect of the addition of very small amounts of HCl is most conveniently explained by its high adsorbability. Duclaux chooses to explain these poisoning effects by actual chemical reaction of the electrolyte with ferric ions that are present. Such can hardly be the case for this would make it difficult to explain the effects of chlorides on the decomposition. Furthermore, such an explanation would not show why the addition of small amounts of HCl decreases the speed of the H_2O_2 decomposition so much more than does the addition of an equivalent amount of chloride ion in the form of NaCl or $BaCl_2$.

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[1] Spring: Bull. Acad. roy. Belg., (3) 30, 32 (1895).

Moreover, Sorum has shown that iron oxide sols, prepared and tested as the sol used in the present investigation, do not contain more than 0.0001692 grams of chloride ion per liter calculated as HCl. Choosing the conditions and results of the first run in Table IV as a typical example of a determination in which no electrolyte was added the following calculation can be made. In that run 3.29 cc. of sol were used in 21.66 cc. of reaction solution. Thus the most $FeCl_3$ that could be present in this reacting solution would be $\frac{0.0001692 \times 35.46 \times 3.29}{3 \times 35.46 \times 21.66 \times 36.47} = 234.9 \times 10^{-9}$ mols of $FeCl_3$ per liter. Bohnson[1] has found that the time of half life of an H_2O_2 decomposition at 25° catalyzed by 0.002974 mols of $FeCl_3$ per liter is about 9 minutes. Now 234.9×10^{-9} would have to be doubled about 13 1/2 times in order to give a concentration of 0.002974 mols per liter. As has been determined earlier in this investigation doubling the concentration of the catalyst increases the velocity of decomposition about 2.2 times or divides the time of half life, which was 56 minutes for the particular run under discussion, by 2.2. Then if the concentration of the catalyst was doubled 13 1/2 times the time of half life would be divided by 2.2 thirteen and one half times. But this reaction was run at 50° and Bohnson's results are for 25°; hence the time of half life would have to be multiplied by the ten degree temperature coefficient about 2 1/2 times to make it apply at 25°. The temperature coefficient has already been determined to be about 2.3 which is roughly the same as 2.2 so that dividing by 2.2 thirteen and one half times and then multiplying by 2.3 two and one half times would be roughly the same as dividing by 2.2 eleven times. Dividing 56 by 2.2 eleven times gives 0.0096 minutes as the time of half life of H_2O_2 in a solution of catalyst containing not more than 0.002974 mols of $FeCl_3$ per liter. But this makes the solution of this catalyst containing not more than 0.002974 mols of $FeCl_3$ per liter about 1000 times as active as a solution containing 0.002974 mols of $FeCl_3$ per liter without any colloid being present so that most of the decomposition in this investigation must be attributed to particles of colloidal ferric oxide and not to the possible traces of ferric ions that may be present as $FeCl_3$.

The writers do not claim that, in cases such as those used by Duclaux and by Bredig and von Berneck where appreciable amounts of $FeCl_3$ still remain in the sol, some of the decomposition is not caused by ferric ions; but they do feel that the above investigators are mistaken when they say that colloidal particles of ferric oxide cause none or practically none of the reaction. Also it seems quite likely that the poisoning effects of K_2SO_4 and $K_4Fe(CN)_6$ noted by Duclaux are due mostly to the adsorption of these electrolytes on the colloidal iron oxide and not to their chemical reaction with the $FeCl_3$ that is present.

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[1] Bohnson: J. Phys. Chem., **25**, 19 (1921).

On the other hand, the writers do not maintain that the solid colloidal particles of ferric oxide are the actual catalyst. It seems entirely possible that some intermediate compound may be formed which serves as the catalyst. Bohnson regarded the decomposition of H_2O_2 by ferric ions as being due to the formation of ferric acid which served as the intermediate compound. In the light of his work a similar reaction mechanism could be advocated for the decomposition of H_2O_2 by colloidal particles of ferric oxide. In such a case the reaction could be represented by the following equations:

$$Fe_2O_3 + 3\ H_2O_2 \rightleftharpoons 2\ H_2FeO_4 + H_2O$$

$$2\ H_2FeO_4 + 3\ H_2O_2 \longrightarrow Fe_2O_3 + 5\ H_2O + 3\ O_2.$$

No doubt the colloidal particles of iron oxide are somewhat hydrated so that more H_2O should be included in the above equations but this would not essentially change the mechanism.

No important objections to the above method of representing the reaction seem to present themselves. It is quite probable that the ferric acid formed remains adsorbed on the colloidal particles of iron oxide, so that when it is decomposed the surface of the micelles remains essentially unchanged. Such an action would preclude any objections which might maintain that if the colloidal ferric oxide is continually undergoing chemical reactions, such as those represented in the above equations,its physical constitution would soon be changed so much that a corresponding change in the decomposition velocity of the H_2O_2 should be noticed.

So far as the present work is concerned there are no indications that the intermediate compound formed is ferric acid. It could just as well be some higher oxide of iron such as those mentioned by Manchot[1]; namely FeO_2, Fe_2O_5, or FeO_3. The chief difference that this would introduce would be a difference in solubility of the intermediate compound or, in the case of FeO_3, just a difference in hydration. Other investigators have advocated the formation of intermediate oxide films in H_2O_2 decomposition. In fact it seems likely that oxide formation in many such reactions is an important factor. In general those metals which form more than one oxide, for example mercury, copper, gold and iron oxides, are more effective in decomposing H_2O_2 than are other metal oxides. Hence, the writers believe that some intermediate compound containing iron with a higher valence is formed in the present reaction. This work gives no indication as to whether this compound is ferric acid or a higher oxide of iron.

Summary

1. The subject of the catalytic decomposition of hydrogen peroxide by colloidal ferric oxide has been investigated at a temperature of 50° C. and in the dark.

2. The reaction has been found to be approximately an apparent monomolecular reaction.

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[1] Manchot and Wilhelms: Ber., **34**, 2479 (1901); Manchot: Ann., **325** 105 (1902).

3. In general the velocity constants increased as the reaction progressed, especially so at the beginning of the reaction.

4. The average temperature coefficient for a ten degree rise of temperature has been found to be about 2.33 between 30° and 60° C. This temperature coefficient seems to indicate that the reaction velocity is governed by the speed of a chemical reaction rather than by a process of diffusion.

5. The rate of decomposition is multiplied by about 2.2 each time the catalyst concentration is doubled between the limits of 0.286 and 2.281 g. of iron per liter.

6. The effects of additions of $NaCl$, $BaCl_2$, K_2SO_4, NaH_2PO_4, Na_2HPO_4, HCl, $NaOH$, and $CuSO_4$ over a considerable range of concentration have been investigated. In the case of $NaCl$, $BaCl_2$ and K_2SO_4 typical "flocculation curves" have been obtained which show the effects of adsorption of the electrolyte by the colloidal iron oxide, the limits and effects of flocculation of the sol, and finally, the effects of adsorption of the electrolyte by precipitated iron oxide. In the case of the other electrolytes modifications of these flocculation curves were obtained which can be satisfactorily explained by the effects of these various substances on the stability of solutions of H_2O_2.

7. For electrolytes which have little effect on the stability of H_2O_2 this method of procedure can be used for a study of adsorption of the electrolyte by colloidal ferric oxide in the presence of H_2O_2 and for determining the flocculation value of the sol in the presence of H_2O_2.

8. Evidence has been found which indicates that particles of colloidal ferric oxide act as the catalyst and that the effects of addition of various electrolytes are due to their effect on these colloidal particles rather than to a reaction between these and the possible traces of $FeCl_3$ that may be present.

9. A possible mechanism for the reaction, involving the formation of ferric acid or some higher oxide of iron as an intermediate compound, has been proposed.

Madison. Wisconsin.

LIQUID AMMONIA AS A LYOPHILIC DISPERSION MEDIUM. II
AMMONO-GELS OF CELLULOSE ACETATE

BY ROBERT TAFT AND JESSE E. STARECK

In previous papers[1] the senior author has called attention to the fact that liquid ammonia is an excellent dispersion medium for the cellulose esters. Further it was pointed out that in the case of cellulose acetate, gels were formed upon standing at room temperature. This paper deals with the extent of dispersion of cellulose acetate in liquid ammonia, the chemical action of the solvent upon this substance and lastly some of the properties of two types of gels formed by this system.

The cellulose acetate used in the investigation was that manufactured by the Eastman Kodak Co. which was air dried at 100°C before use. It is probably a mixture of acetates up to the triacetate. The product now marketed by this organization as cellulose triacetate is not so readily dispersable as is the product of lower acetylation.

The ammonia used was in some cases drawn directly from a cylinder of anhydrous liquid ammonia, the usual precautions being taken to prevent absorption of water. Later, when it became necessary to study the effect of water upon the gelatinization of these systems, the ammonia used was dried over sodium and distilled under slight excess pressure in a closed train into the tube containing the cellulose acetate, which was cooled by an external bath of the same liquid. In most cases observations were made with the samples under examination sealed in tubes of pyrex in order to continue the observations at higher temperatures than the boiling point of liquid ammonia (−33.5°C).

Dispersability

Apparently there is no limit to the dispersability of cellulose acetate in this liquid. Ammonosols ranging from very dilute ones up to 60 grams of cellulose acetate in 100 cc. of the dispersion medium have been prepared.[2] Higher concentrations can be obtained but the concentrations above this limit are difficult to estimate and the systems are so gummy and plastic that they are exceedingly difficult to work. In order to obtain these gels of higher concentration the following conditions must be observed: (a) low temperature must be maintained; it is necessary in order to secure dispersion, that the temperature of the system be in the neighborhood of boiling ammonia (−33.5°C); (b) considerable mechanical agitation must be employed in order to secure the necessary circulation of the liquid and to secure as large a surface of contact as possible between the two phases. The latter was secured by stirring with a glass rod while the acetate was being added. In order to obtain the highest concentrations of the sol mentioned above it was necessary to evaporate a sol containing 30 grams of acetate per 100 cc. of solvent to one-half of its original volume.

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[1] Taft: J. Phys. Chem., 34, 2792 (1930); Trans. Kansas Acad. Sci. 32, 58 (1929). Clancy, U. S. Patents 1,544,809 and 1,544,812 (1925), has covered the dispersability of cellulose nitrates and acetates with patents but no information is given upon the properties of such systems as herein described; Fenton and Berry (Proc. Camb. Phil. Soc., 20, 16 (1920)) were the first to point out that cellulose acetate disperses in liquid ammonia.

[2] In order to save words we have referred to our concentrations in terms of per cent. This is a misnomer but a 60% system means one containing 60 grams of cellulose acetate per 100 cc. of dispersion medium, etc.

Sols containing 1% or less of cellulose acetate were clear, colorless, mobile liquids. The viscosity was increased considerably over that of the pure dispersion medium and was a function of time, particularly at room temperature. When the sealed tubes were allowed to warm up to room temperature, the viscosity rapidly decreased at first but after a few hours began to increase again. This increase in viscosity, as will be shown, is due to a change in the composition of the dispersed phase. On the whole it may be said that the viscosities of these systems are affected by concentration, temperature, and age as is the case with many other lyophilic systems.

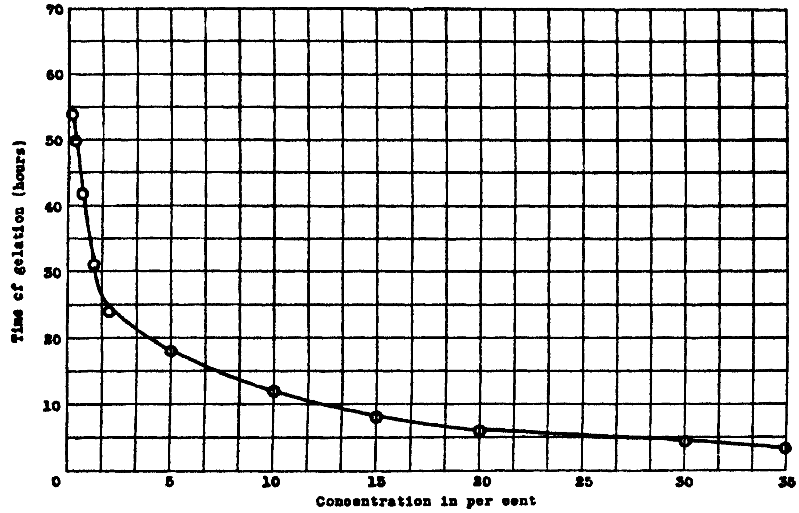

Fig. 1
Time of gelation as a function of concentration of cellulose acetate. Irreversible Gels.

Sols of higher concentration were very viscous, translucent, but of light brown color.

Heat Irreversible Gels

As was stated above, the ammonosols when allowed to warm to room temperature (ca 25°C) decreased in viscosity at first, but after several hours the viscosity increased, the system eventually setting to a gel. The gels thus formed were white opaque masses and did not redisperse when recooled to the temperature of boiling ammonia, i.e. they were heat irreversible. In one case the gel which had formed at room temperature was recooled in boiling ammonia and kept at that temperature for several weeks without indication of melting of the gel. The time necessary for gelation was found to be a function of the concentration, the temperature, and the water content of the dispersion medium. Table I and Fig. 1 give the time of gelation as a function of the concentration of the cellulose acetate.

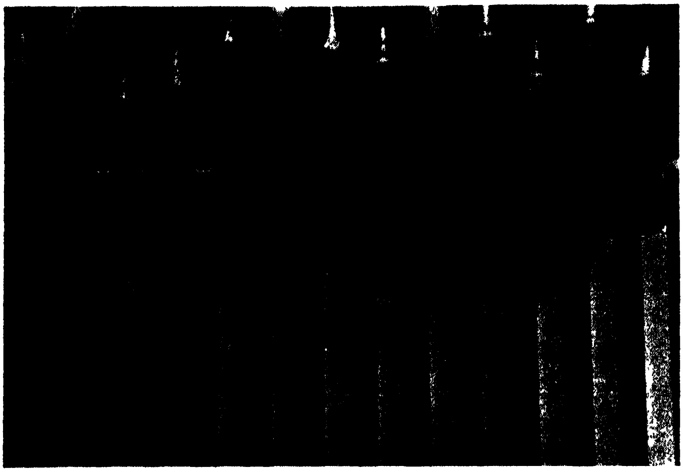

FIG. 2
Heat Irreversible Gels.
Tubes left to right have cellulose acetate content of:
0.0% 0.05% 0.1% 0.2% 0.3% 0.5%
1% 2% 5% 7.5% 10% 15% 20%

TABLE I

Conc. of cellulose acetate %	Time of Gelation Hours	Appearance of Gel
0.1	54	Soft clear gel; marked syneresis
0.2	46	Firm translucent gel; marked syneresis
0.5	38	
1.	31	Striated; some syneresis
2.	24	Vertical crack; some syneresis
5.	18	Opaque, rigid, white; "Sine curve" crack; syneresis apparent
10.	12	
15.	8	Striated; oblique cracks; marked syneresis of brown liquid; gel contracted.
20.	6	
30.	4.5	
35.	3.5	

The appearance of the gels is also recorded photographically in Fig. 2, the gels here depicted being approximately two weeks old. The time of gelation as a function of temperature is shown graphically in Fig. 3, the temperatures of observation being the boiling temperature of ammonia, the ice point and room temperature. In the case of the 5% gel the system was kept at −33.5°C for two weeks, the sol becoming slightly cloudy in that time but gelation did not occur. On removing it from the bath and allowing it to warm to room temperature, gelation occurred in eight hours or about one-third of the normal time. As will be shown, gel formation occurs as a result of chemical action, and consequently it was assumed that two-thirds of the reaction had taken place and it is upon this basis that we have plotted the point at −33.5°C. In the case of the 10% gel, a gel formed at the boiling point of ammonia within a few hours but this proved to be of the heat-reversible type described later. On warming, it melted and set to the irreversible type in about the usual time. This seems unusual for the more concentrated system would be expected to set more quickly, but apparently the reversible gel structure prevented the reaction between disperse phase and dispersion medium from proceeding so rapidly, i.e. the disperse phase is not in as intimate contact in the gel state as when in the sol form, for in the gel state most of the dispersion medium would be present in the gel pores.

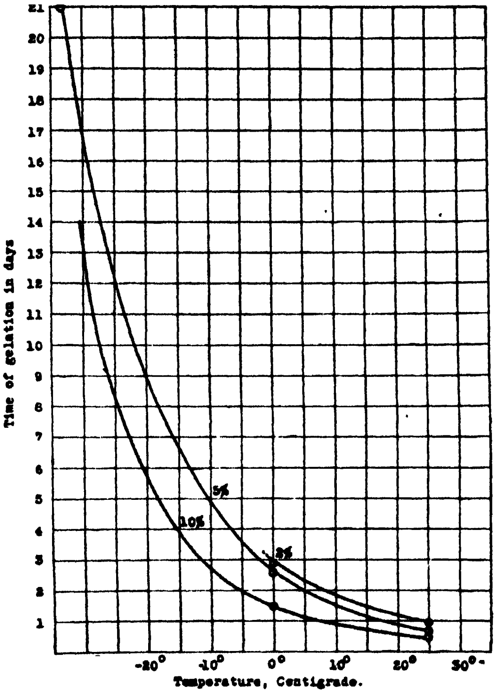

Fig. 3
Time of gelation as a function of temperature. Irreversible Gels.

In the more dilute gels considerable difficulty was at first experienced in obtaining concordant data on the time of setting for a gel of a given concentration. This was finally traced to the presence of small but variable quantities of water present in the dispersion medium. This led us to investigate the effect of water upon the dispersability of the acetate and upon the properties of the gels thus formed. Known quantities of water were added to ammonia distilled from sodium. Under these conditions results were obtained which were reproducible for dilute sols but for those more concentrated than 0.5% dispersion did not take place quickly enough to obtain a uniform system by simply shaking the tube containing the materials under examination. The data recorded in Table II and graphically in Fig. 4 shows the effect of varying quantities of water upon the structure of the gel and the time of gelation. Fig. 5 shows photographically the results at a concentration of 0.1% cellulose acetate.

The facts to be noted in connection with the effect of water are: (a) dispersion of small quantities of cellulose acetate can take place in the presence of large quantities of water;[3] (b) precipitation and not gel formation takes

TABLE II

Gels formed in the Presence of Water

Amount of H_2O	Time of Setting	Structure
	0.5% Cellulose Acetate	
None	38 hours	Coarse gel, gradually settling
1%	32	Slightly grainy gel
2%	27	Fine gel
5%	20	Fine opalescent gel
	0.2% Cellulose Acetate	
None	46 hours	Gelatinous precipitate
1%	36	Coarse, granular gel
2%	28	Fine gel
5%	22	Fine, opalescent gel
	0.1% Cellulose Acetate	
None	54 hours	Flocculent precipitate
1%	42	opalescent gel
2%	26	Precipitate
5%	21	Gelatinous precipitate
10%	15	Grainy, coarse gel
	0.05% Cellulose Acetate	
None	41 hours	Precipitate
0.5%	41	Precipitate
1%	35	Opalescent, soft gel
2%	25	Precipitate
5%	17	Precipitate
10%	9	Gelatinous precipitate
20%	3-6	Precipitate

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[3] The range of dispersability is not great in the presence of large quantities of water, however. Thus a system containing 25% water and 0.1 gm. of the acetate to 100 cc. of dispersion medium showed no appreciable dispersion.

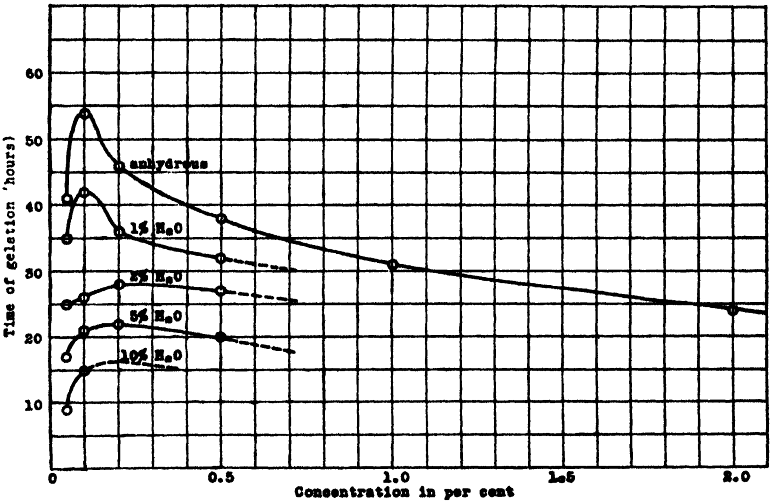

Fig. 4
Effect of Water on Time of Gelation. Irreversible Gels.

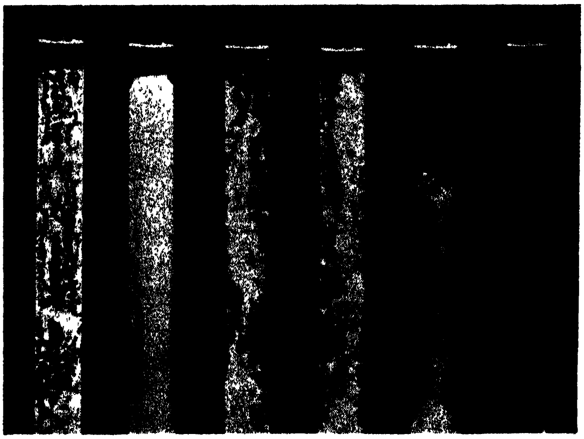

Fig. 5
Effect of Water Content on Gel Structure.
Cellulose acetate content 0.1%.
Tubes left to right have water content of:
0.0% 1% 2% 5% 10%
Tube on extreme right is pure ammonia.
The gels are not so opaque as these photographs would indicate.

place in the absence of water; (c) gels form more rapidly and are of firmer structure at an optimum value of water concentration; (d) very minute concentration of the acetate can produce gels. In connection with the last point it can be said that the lower limit of concentration of gel formation is at least as low as 0.05 per cent (rather 0.05 per 100 cc. of ammonia). This is probably the lowest concentration at which gelation has been recorded. Weiser[4] produced aqua-gels containing 0.09 per cent chromic oxide. Kruyt[5] states that an aqueous system containing 0.14% agar will gel at room temperature. As far as the writers are aware these are the lowest concentrations previously recorded for gel formation in other systems.

One striking peculiarity of these gels was observed, particularly in gels containing 7.5% of cellulose acetate. This was the development of cracks of very regular form, which we have termed "sine curve" breaks. These are shown photographically in Fig. 6; they were not restricted to gels of this particular concentration but characterized gels from 5 to 10%, appearing in from one to two days after gelation, depending upon the previous history of the sample. The "wave length" of these curves was found to be a function of the bore of the tube as shown in the illustration. These breaks are undoubtedly caused by the gel's contraction which begins shortly after gelation, but since the exterior surface of the gel adheres to the glass wall a strain within the gel is produced. As contraction proceeds, the stress produced finally becomes sufficient to rupture the structure. Since the structure is thinner near the walls of the tube it will tear there first as resistance to strain is proportional to cross sectional area, but also, as the membrane becomes thinner, it will stretch more for a given load, or stress; consequently the stress is relieved on this side before the break reaches the edge. But the stress on the other side must also be relieved since it is now greatest and a break is then produced in this region. The original production of strain is characterized by an absorption of all of the liquid of syneresis, giving the surface of the gel a dry appearance. After the completion of the break, however, syneresis takes place a second time.

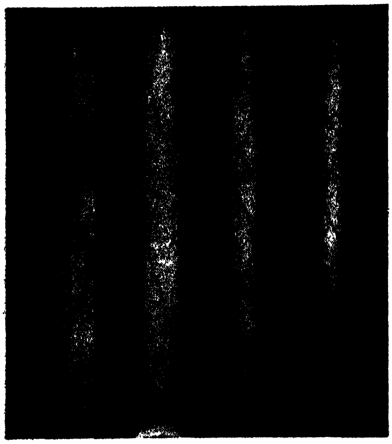

FIG. 6

We have observed the production of somewhat similar breaks in silica aqua-gels but never so regular as here shown. In fact we have noticed many points of similarity between these ammono-gels of cellulose and aqua-gels of silica. In external appearance they are very much alike; they are both heat irreversible; further the time of gelation is a somewhat similar function in both cases.[6] Freshly prepared gels of higher concentration vibrate also when struck, as do silica gels.

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[4] J. Phys. Chem., 26, 431 (1922).

[5] "Colloids," 169 (1927).

Evidence of Chemical Change in Heat-Irreversible Gels

A number of tubes containing gels were recooled in liquid ammonia, opened and the gels removed for examination. The 5 per cent gels were quite rigid and brittle, but shrank rapidly and increased in toughness as the ammonia evaporated. A gel four inches by one-half inch diminished in size to one inch by one-eighth inch, leaving a yellow transparent residue, which did not swell or disperse again when placed in liquid ammonia. Further this horn-like structure was not only inert toward ammonia but also to all liquids which disperse cellulose acetate. Hydrochloric acid had no effect upon it and concentrated sulfuric acid only softened it slightly in a few hours; the original cellulose acetate is rapidly attacked by these acids. These gel residues are dispersed, however, by Schweitzer's reagent. Apparently the material comprising the gel structure is cellulose, i.e. the dispersion medium reacts with the cellulose acetate converting it to cellulose. In the absence of any water in the dispersion medium, acetamide would likely be formed in addition to cellulose. In the presence of water ammonium acetate would be the most probable second material. To test this point out a gel was prepared and allowed to synerize. The tube was then cooled, opened and the synerized liquid removed. This liquid was then added to water (it produced no residue) and tested qualitatively by adding amyl and ethyl alcohols to separate tubes containing the above liquid in dilute sulfuric acid. The characteristic odors of banana oil and ethyl acetate were easily detected.

It will be recalled that for dilute concentrations of cellulose acetate, the best gels were formed in the presence of water. This would seem to indicate that traces of water are necessary for gel formation. That it is not solely a case of reaction is evident from a consideration of the data of Table II. If it be assumed that the reaction

$$[C_{12}H_{18}O_8(COOCH_3)_6]_x + 6H_2O = [C_{12}H_{24}O_{12}]_x + 6CH_3COOH$$

takes place, the mass of cellulose acetate is roughly five times that of the water involved. From Table II, 0.05 gram of cellulose acetate requires 1% of water to produce the best gel, whereas 0.5 gram of cellulose acetate requires 2 to 5% water to produce the best gel, i.e. relatively more water is required in the case of the dilute gels. It would appear that the gel structure is dependent upon *adsorbed* water to secure the firmest gel.

Diffusion Experiments

The ammono-gels thus described make suitable systems for diffusion experiments. We have not tried a great number of these but have carried out a few experiments with liquid ammonia solutions of sulfur in the hope that some information on the colloidity of these systems could be obtained. An inverted Y tube with the ends of the lateral branches sealed was made, so that the cellulose acetate sol could be placed in one branch and the sulfur solution in the other. The tube was then sealed, brought to room temperature and the gel allowed to set. The sulfur solution was then added to the top of the gel by tipping. Diffusion took place rapidly at the rate of about two inches in twenty-four hours. This rapid diffusion might indicate that a considerable proportion, if not all, of the sulfur was present in true solution. It was found necessary to carry these diffusion experiments out in the dark as the sulfur solutions were reversibly light sensitive, turning pale yellow in the light and deep blue in the dark. In fact the reversals on one specimen were carried out a number of times without any apparent effect on the sulfur.

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[6] For example, Holmes (J. Phys. Chem., **22**, 510 (1918)), showed that the time of setting of a silica aqua-gel was greatly increased at 0°C and decreased with rising temperature on curves similar in form to those shown in Fig. 3.

Heat-Reversible Gels

As was stated previously, when the 10 per cent sol of cellulose acetate was placed in an ammonia bath for several days a gel structure appeared. This led to the investigation of the possibility of gel formation of a heat-reversible type upon cooling the ammonia below its boiling point. Reversible gels of cellulose acetate have been prepared in benzyl alcohol by Mardles[7] and Poole,[8] consequently one might expect an analogous system in liquid ammonia.

Samples of 5 and 10 per cent cellulose acetate were prepared and cooled in a bath of gasoline to which had been added solid carbon dioxide with the result that at $-45°$ C the 10 per cent sol changed to a beautiful opalescent gel which was quite rigid and brittle with an elasticity similar to that of gelatin gels. The color was also less intense for a given concentration than it was in the irreversible type. The 5 per cent sol remained fluid until a temperature of $-60°$C was reached, when a similar opalescent gel appeared. Thus it will be seen that the higher the concentration of the gel, the higher its temperature of gelation—a characteristic of heat-reversible gels such as agar or gelatin in water and cellulose acetate in benzyl alcohol.

On warming up the bath gradually, it was found that the gels would not melt at the same temperature at which they jelled, but a temperature of about ten degrees higher was necessary to bring about this change. This is similar to what Poole[8] found in studying cellulose acetate in benzyl alcohol and is generally characteristic of heat-reversible gels.

The above observations were made on samples sealed in pyrex tubes which were afterwards allowed to warm up to room temperature. The sols become more fluid at first but later set to the heat-irreversible type of gel previously described. The characteristic sine curve break already noted for gels of these concentrations formed in about twenty-four hours after gelation with the usual syneresis following.

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[7] Trans. Faraday Soc., **18**, 318 (1922).

[8] Trans. Faraday Soc., **22**, 140 (1926).

Summary

1. Cellulose acetate will disperse in liquid ammonia apparently without limit. Sols as concentrated as 60 per cent have been obtained.

2. Ammono-sols of cellulose acetate present the unique case of forming two types of gels, one type being heat reversible; the second heat-irreversible.

3. The heat-irreversible gels, apparently consist of a structure of cellulose which has adsorbed water.

4. Heat-reversible gels may be obtained by cooling the ammono-sols to low temperatures. The setting points of these gels was found to be lower than their melting points, a phenomenon which is of common occurrence in reversible gels.

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THE POTENTIAL OF THE CADMIUM ELECTRODE

BY FREDERICK H. GETMAN

In a recent study of the copper electrode[1] it was pointed out that a single crystal of pure copper functions as a constant and reproducible electrode when immersed in solutions of copper sulphate. Shortly after the paper embodying the results of our experiments on the copper electrode was written, Anderson[2] published an account of his investigation of the electromotive behavior of single crystals of zinc. He measured air-free cells of the type

$$\mathrm{Zn,\ ZnCl_2(aq),\ Hg_2Cl_2,\ Hg,}$$

and employed fifteen crystals prepared by three different methods. He shows conclusively that a single crystal of pure zinc behaves as a "reversible electrode capable of yielding potentials constant to a few hundredths of a millivolt and reproducible over dissimilarly prepared crystals to one or two-tenths of a millivolt." While Anderson's measurements were made with especial reference to the constancy and reproducibility of the potential of the primary cleavage, or (0001) face, of the zinc crystal, he also showed that "a cylindrical section of a crystal parallel to its major axis, containing along with the (0001) face, sharp edges and orientations other than the (0001) face, gives the same equilibrium potential as the isolated basal planes."

More recently, Straumanis[3] in a study of the electrochemical behavior of single crystals of zinc has found that the cleavage planes of a single crystal when immersed in a neutral solution of zinc sulphate always give rise to the same average difference of potential, and that the latter is in agreement with the difference of potential developed by immersing a polycrystalline electrode of pure zinc in the same solution.

In view of the foregoing results it seemed of interest to study in a somewhat similar manner the electromotive behavior of single crystals of cadmium.

The measurements of Horsch[4] on the cell

$$\mathrm{Cd(amalgam),\ CdCl_2(aq),\ AgCl(electrolytic),\ Ag,}$$

undoubtedly afford the most accurate available data upon which to base calculations involving the potential of the cadmium electrode. Measurements of the cell

$$\mathrm{Cd,\ CdCl_2(aq),\ Hg_2Cl_2,\ Hg,}$$

recently made by the writer,[5] while substantially in agreement with the data of Horsch, are inadequate for the calculation of the electrode potential of cadmium because of the fact that the values of the electromotive force in the more dilute solutions were manifestly too low.

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[1] Getman: J. Phys. Chem., **34**, 1454 (1930).

[2] Anderson: J. Am. Chem. Soc., **52**, 1000 (1930).

[3] Straumanis: Z. physik. Chem., **147**, 161 (1930).

[4] Horsch: J. Am. Chem. Soc., **41**, 1787 (1919).

[5] Getman: J. Phys. Chem., **32**, 91 (1928).

Experimental

Materials. Cadmium chloride of a high degree of purity was subjected to recrystallization before making up the mother solution.

All of the mercurous chloride used in the cells was prepared according to the electrolytic method of Hulett.[1]

Redistilled mercury was further purified by distillation in a current of air as recommended by Hulett.[2]

The single crystals of cadmium were prepared for the writer by Mr. J. H. Dillon of the University of Wisconsin according to the method recently developed by him for the preparation of single crystals of metals of low fusibility.[3] The purity of the metal from which these crystals were prepared is indicated by the following analysis: Cd 99.944%, As 0.001%, Fe 0.005%, Pb 0.050%. The polycrystalline electrodes were made either from cadmium especially purified for use in standard cells, or from so-called "spectroscopic" cadmium, kindly furnished us by Mr. H. M. Cyr of the Research Laboratory of the New Jersey Zinc Co. and guaranteed to contain not more than 0.001% of impurity.

The spark spectra of the cadmium from these three different sources when compared by means of a Hilger quartz spectrograph, failed to reveal the presence of more than a trace of foreign metals.

All of the water used in making up the solutions was prepared by redistilling ordinary distilled water with chromic acid and condensing in a block tin condenser. The water was stored in tightly stoppered bottles of Jena glass.

The nitrogen which was used to displace air from the electrolyte in the cells was obtained in cylinders and was purified before entering the cells by passing through aqueous solutions of potassium permanganate, alkaline pyrogallol, water and cadmium chloride of the same concentration as that in the cells.

Apparatus. The apparatus employed was the same as that used in our previous study of the copper electrode[4] and the same experimental procedure was followed both in setting up the cells and measuring their electromotive force.

Preparation of Electrolyte. A stock solution of cadmium chloride was prepared by dissolving a mass of the recrystallized salt in conductivity water sufficient to make a solution of approximately molal concentration. To this was added a small amount of pure cadmium hydroxide, after which the solution was shaken at frequent intervals over a period of several days. After standing until the excess of hydroxide had settled, the chlorine content of the solution was determined gravimetrically as silver chloride. A simultaneous determination of the density of the solution with an Ostwald pyknometer supplied the necessary data for the calculation of its molality. This was found to be 0.99472 M. The solutions of smaller concentration were prepared by dilution in calibrated volumetric apparatus.

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[1] Hulett: Phys. Rev., (2) **32**, 32 (1900).

[2] Hulett: Phys. Rev., (2) **33**, 307 (1901).

[3] Dillon: Rev. Sci. Inst., **1**, 36 (1930).

[4] Loc. cit.

Electromotive Force Measurements

Immediately after setting up, the cells were immersed in the thermostat bath and their electromotive forces were measured, after allowing sufficient time for the establishment of thermal equilibrium. The measurements were continued at frequent intervals over a period of six hours. During this time the cells maintained a satisfactory constancy of electromotive force, except in the case of those in which the electrolyte was dilute. With the latter there was an increasing tendency toward a slight but steady drift in the electromotive force. The electrodes prepared from the highly purified "spectroscopic" cadmium were prone to exhibit erratic fluctuations of potential over a range of several tenths of a millivolt. The single crystal electrodes, however, did not show this tendency to fluctuation and proved to be almost as steady as cadmium amalgams. The experimental data given in Table II represent the mean of ten or more measurements of the electromotive force at each concentration. The electromotive force of six cells containing electrodes of either "spectroscopic" or "standard cell" cadmium is denoted by E_1 while that of two cells containing single crystals of cadmium as electrodes is denoted by E_2. In view of the statements of both Anderson and Straumanis, it was not deemed necessary to split the single crystals along their cleavage planes in order to expose only a single definite surface to the electrolyte. Because of the relative instability of cells in which the electrolyte is dilute, no attempt was made to measure electromotive forces in solutions having a concentration less than 0.01M.

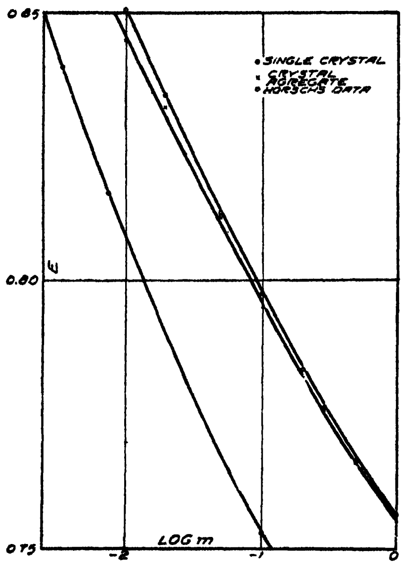

FIG. 1

It is apparent that the numerical value of the potential of the single crystal electrode is uniformly greater than that of the polycrystalline electrode. This result is similar to that obtained in our study of the copper electrode. The foregoing values, believed to be accurate to within 0.3 millivolt, are represented graphically in Fig. 1. By means of a large scale plot, similar to Fig. 1, the values of the electromotive force at even concentrations were read from the curves and tabulated in Table II.

TABLE I

Measurements of the E.M.F. of the Cell
Cd, $CdCl_2$(m), Hg_2Cl_2, Hg at 25°

m mols $CdCl_2$/1000 g. H_2O	E_1	E_2
0.00966	0.84652	0.85021
0.04805	0.81165	0.81258
0.09986	0.79542	0.79758
0.20027	0.78208	0.78390
0.28766	0.77628	0.77641
0.49084	0.76625	0.76636
0.99472	0.75554	0.75646

TABLE II

Smoothed Values of the E.M.F. of the Cell
Cd, $CdCl_2$(m), Hg_2Cl_2, Hg at 25°

m mols $CdCl_2$/1000 g. H_2O	E_1	E_2	ΔE
0.01	0.8435	0.8515	0.0080
0.02	0.8290	0.8340	0.0050
0.05	0.8097	0.8120	0.0023
0.1	0.7953	0.7973	0.0020
0.2	0.7820	0.7835	0.0015
0.5	0.7660	0.7675	0.0015
1.	0.7553	0.7563	0.0010

Calculation of Results

In order to calculate the normal electrode potential of cadmium, E_0, from the data of Table II, it is necessary to have recourse to the extremely accurate data obtained by Horsch with cells in which the electrolyte was very dilute. In his calculations, Horsch made use of the best available conductivity data and assumed that in extremely dilute solutions of cadmium chloride the values of the conductivity ratios are equal to the corresponding values of the activity coefficients. Quite recently, Randall[1] has developed a convenient method of extrapolation for the determination of normal electrode potentials from electromotive force data. Employing this method, we have recalculated the normal electrode potential of cadmium from Horsch's data. Having thus computed the value of E_0, the activity coefficients of cadmium chloride at different concentrations can readily be calculated and from these in turn, the potential, E_0, corresponding to the single cadmium crystal electrode can be evaluated.

The electromotive force of the cell

Cd, $CdCl_2$(m), AgCl, Ag,

studied by Horsch, can be computed by means of the equation

$$E = E_0' - \frac{RT}{nF} \ln (4\, m^3\, \gamma^3) \tag{1}$$

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[1] Randall: Trans. Faraday Soc., **23,** 505 (1927).

In this equation E is the measured electromotive force of the cell, E_0' th normal potential of the cell, m the concentration in mols per 1000 grams o solvent and γ is the activity coefficient. The symbols R, T, n and F have their usual significance. Simplifying and transforming to common logarithms, equation (1) takes the form

$$E = E_0' - 0.08873 \log (1.588 \text{ m } \gamma). \tag{2}$$

Following the method of Randall, equation (2) may be transformed into

$$\log \gamma - E_0'/0.08873 = -(E/0.08873 + 0.2007 + \log \text{m}) \tag{3}$$

If the right-hand side of equation (3) be plotted against the square root of the ionic strength, μ, and the resulting curve be extrapolated to infinite dilution, the value of E_0' can readily be calculated by means of equation (3).

The experimental data of Horsch are reproduced in Table III and a partial graphic representation is given in Fig. 1.

TABLE III

Horsch's Measurements of the E.M.F. of the Cell

Cd, $CdCl_2$(m), AgCl, Ag at 25°

m	E	m	E
0.0001029	0.9594	0 0003659	0.9148
0.0001087	0.9557	0 000479	0.9050
0.0001137	0.9545	0.000924	0.8830
0.0001269	0.9512	0 002581	0.8491
0.0001527	0.9460	0.003519	0.8398
0.0002144	0.9337	0.0074	0.8165
0.0003363	0.9178	0.0995	0.7530

The data of Table III were plotted on a large-scale plot and the values of E corresponding to log m = $\bar{6}.0$, log m = $\bar{6}.1$, log m = $\bar{6}.2$, etc. up to log m = $\bar{7}.0$ were read from the curve and tabulated, together with the corresponding values of $\mu^{\frac{1}{2}}$ and (E/0.08873 + 0.2007 + log m) as shown in Table IV.

TABLE IV

Data derived from Horsch's Measurements

m	$\mu^{\frac{1}{2}}$	E	(E/0.08873 + 0.2007 + log m)
0.0001000	0.01732	0.9597	7.0107
0.0001259	0.01943	0.9523	7.0407
0.0001585	0.02181	0.9445	7.0407
0.0001995	0.02446	0.9365	7.0507
0.0002512	0.02745	0.9282	7.0607
0.0003162	0.0308	0.9199	7.0707
0.0003981	0.0346	0.9117	7.0807
0.0005012	0.0388	0.9035	7.0807
0.0006310	0.0435	0.8954	7.0907
0.0007943	0.0488	0.8876	7.1007
0.001	0.0548	0.8801	7.1197

On plotting the values of $(E/0.08873 + 0.2007 + \log m)$ versus $\mu^{\frac{1}{2}}$, as shown in Fig. 2, the averaged straight line through the points thus obtained intersects the zero ordinate at a point corresponding to 7.005. On substituting this value in equation (3), we find $E_0' = 0.6215$ volt, the normal potential of the cell.

In order to determine the normal electrode potential of cadmium, Horsch also measured the electromotive force of the cell

$$H_2 \text{ (1 atm.)}, HCl(0.01M), AgCl, Ag,$$

and found E = 0.4665 volt. Accepting 0.93 as the value of the activity coefficient of 0.01M HCl, we have

$$\begin{aligned} E_0 &= 0.4665 + 0.05915 \log (0.01 \times 0.93) \\ &= 0.2283 \text{ volt,} \end{aligned}$$

or

$$H_2, H^+ (M), Cl^- (M), AgCl, Ag;\ E_0 = 0.2283 \text{ volt.}$$

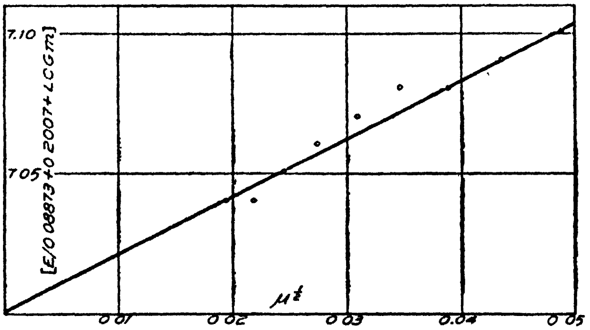

FIG. 2

Hence Horsch's value of the normal electrode potential of cadmium is

$$\begin{aligned} E_0 &= 0.6215 - 0.2283, \\ &= 0.3932 \text{ volt.} \end{aligned}$$

Horsch actually obtained, as the result of his calculations based upon conductivity data, $E_0 = 0.3992$ volt.

Accepting 0.3932 volt as the value of E_0, we may now proceed to calculate the values of the activity coefficients of solutions of cadmium chloride by means of equation (2). The values of γ thus obtained together, with the corresponding conductivity ratios derived by Noyes and Falk[1], are given in Table V.

In Table V values of γ are slightly less than those calculated by Lewis and Randall[2] from the experimental data of Horsch. This lack of agreement is to be traced to the fact that Lewis and Randall apparently based their calculations on Horsch's observed values of the electromotive force of the cell

$$Cd(4.5 \text{ amalg}), CdCl_2(m), AgCl, Ag,$$

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[1] Noyes and Falk: J. Am. Chem. Soc., **34**, 475 (1912).

[2] Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances", 362.

rather than on the calculated values of the electromotive force of the cell,

$$\mathrm{Cd,\ CdCl_2(m),\ AgCl,\ Ag.}$$

The difference of 0.0534 volt between the electromotive forces of the two cells obviously represents the electromotive force of pure cadmium against the cadmium amalgam. When allowance is made for this difference, their values for γ are in close agreement with those given in Table V. A comparison of the values of γ and α shows that Horsch was not justified in assuming the equality of these two ratios, even in dilute solutions of cadmium chloride.

TABLE V

Activity Coefficients of Cadmium Chloride Solutions (25°)

m	E	γ	α
0.0001	0.9567	0.969	0.975
0.0002	0.9360	0.898	0.960
0.0005	0.9050	0.802	0.931
0.001	0.8810	0.748	0.891
0.002	0.8573	0.690	0.830
0.005	0.8280	0.592	0.735
0.01	0.8085	0.491	0.664
0.02	0.7910	0.389	0.580
0.05	0.7688	0.277	0.453
0.1	0.7535	0.205	0.375
0.2	0.7390	0.149	0.308
0.5	0.7209	0.096	—
1.0	0.7080	0.067	—

We are now in possession of the necessary data for the calculation of the normal electrode potential of the single crystal cadmium electrode. Thus, on substituting the values of γ given in Table V, and the corresponding values of E from Table II, in equation (2) the value of E'_0 can be calculated. The data resulting from this calculation are collected in Table VI.

TABLE VI

Values of E'_0 for the Cell

$\mathrm{Cd(single\ cryst.),\ CdCl_2(m),\ Hg_2Cl_2,\ Hg}$

m	E		E'_0
0.01	0.8515	0.491	0.6645
0.02	0.8340	0.389	0.6648
0.05	0.8120	0.277	0.6649
01.	0.7973	0.205	0.6654
	Mean		0.6649

The mean value of E'_0 is thus found to be 0.6649 volt. Since, according to Gerke[1] the potential of the electrode

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[1] Gerke: Chem. Rev., 1, 384 (1925).

$$\mathrm{Hg,\ Hg_2Cl_2\ (s),\ Cl^-},$$

is −0.2700 volt, it follows that

$$\mathrm{Cd(s),\ Cd^{++};\ E_0 = 0.3949\ volt.}$$

This value for the normal electrode potential, it will be observed, is nearly 3 millivolts less than the value assigned by Gerke[1] to this constant, viz. 0.3976 volt. Presumably, however, Gerke accepted the results of the calculations of Lewis and Randall based upon Horsch's data.

If the values of E in Table II be substituted successively in equation (3) and the resulting values be plotted against the corresponding values of $\mu^{\frac{1}{2}}$, an approximate value of E'_0 can be obtained by graphic extrapolation. Employing this method, we found $E'_0 = 0.6645$ volt, or $E_0 = 0.3945$ volt.

Since single crystals of copper, zinc and cadmium have been found to function as constant and reversible electrodes, it seems reasonable to base our calculations of normal electrode potentials upon measurements of the electromotive force of suitable galvanic combinations in which single crystals of these metals are employed as electrodes. As the result of such calculations based upon the foregoing experimental data, we are led to accept, as the value of the normal electrode potential of cadmium, $E_0 = \mathbf{0.395}$ volt.

Summary

(1) Measurements have been made of the electromotive force of the cell

$$\mathrm{Cd,\ CdCl_2(m),\ Hg_2Cl_2,\ Hg},$$

in which the cadmium electrodes were either single crystals or massive crystalline aggregates of the pure metal.

(2) Single crystals of pure cadmium were found to function as constant and reproducible electrodes.

(3) The numerical value of the potential of the single crystal electrode was found to be uniformly greater than that of the polycrystalline form.

(4) The measured values of the electromotive force of cells with single crystal electrodes were employed to calculate the normal electrode potential of cadmium. The value of this constant has been found to be $E_0 = \mathbf{0.395}$ volt.

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[1] Gerke: Chem. Rev., **1**, 381 (1925).

THE OPTIMUM CONDITIONS FOR THE FORMATION OF SILICA GEL FROM ALKALI SILICATE SOLUTIONS. II

BY R. C. RAY AND P. B. GANGULY

In a previous paper[1] the optimum conditions for the formation of silica gel by the action of hydrochloric acid on solutions of potassium metasilicate and solutions of sodium silicate in which the ratio of $Na_2O:SiO_2$ was as 1:2.25 were determined. It was found that hydrogen ion concentrations were an important factor in the process of gel formation; for each concentration of alkali silicate solution there is a limiting range of pH value in which gel formation takes place. In the present paper the experiments have been extended to the case of two other solutions of sodium silicate in which the ratios of $Na_2O:SiO_2$ are as 1:3.3 and 1:4.0 respectively.

Our knowledge of the alkali silicates is meagre. Two views are prevalent regarding their composition, namely, (1) definite complex silicate ions are produced with increase of the amount of silica in the molecule, and (2) one or two simple silicates are formed and the excess of silica in the molecule of the higher ratio silicates is present as a colloidal aggregate. Schwarz and Menner[2] have obtained definite crystalline compounds of the compositions corresponding to $Na_2O.SiO_2$; $Na_2O.2SiO_2$ and $Na_2O.3SiO_2$ by fusing pure quartz with sodium carbonate at 1150°C. They obtained the last two compounds as glasses which transformed into definite compounds by prolonged heating at 700°C. Morey,[3] by his hydrothermal quenching method, obtained $Na_2O.SiO_2$ and $Na_2O.2SiO_2$ but not $Na_2O.3SiO_2$. A small amount of disilicate also occurs naturally as rivaite[4]. The formation of complex silicic acids has also to be assumed in order to explain the composition of a large number of naturally occurring silicates. On the other hand, Herman, who has recently made a systematic investigation on the nature of alkali silicate solutions, has come to the conclusion that only one or two simple silicates are formed and the extra silica in the higher silicates is mainly present in a colloidal form. Herman's results have been published in this journal between 1925 and 1928 in a series of papers entitled "Aqueous solutions of sodium silicates." If a considerable amount of colloidal silicic acid be present in alkali silicate solutions in which the ratio SiO_2/Na_2O is high, the curves representing the limiting range of pH values between which gel formation takes place might be expected to be of an entirely different type. The present investigation was undertaken with a view to find out if this was actually the case.

The experimental procedure adopted was exactly the same as described in the previous paper. There is for each concentration of the silicate solution a definite range for the pH values beyond which no gelation takes place. The pH values corresponding to the points where gel formation just stopped were accurately measured. The results obtained are given in Tables I and II. Definite volumes of sodium silicate solutions were also previously analysed, and the ratio $Na_2O:SiO_2$ was determined in each case.

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[1] J. Phys. Chem., **34**, 352 (1930).

[2] Ber., **57B**, 1477 (1924).

[3] J. Am. Chem. Soc., **39**, 1174 (1917).

[4] Zambonini: Atti Accad. Sci. Napoli, **12**, 16 (1912).

TABLE I

Showing the region of gel formation for sodium silicate solutions of different concentrations

Ratio of $Na_2O:SiO_2 = 1:3.3$

Mols SiO_2 per litre	Limiting pH (Acid side)	Limiting pH (Alkali side)
0.618	2.18	11.18
0.517	2.30	10.96
0.309	2.86	10.20
0.206	3.46	9.74
0.103	4.01	9.07

TABLE II

Showing region of gel formation for sodium silicate solutions of different concentrations

Ratio of $Na_2O:SiO_2 = 1:4.0$

Mols SiO_2 per litre	Limiting pH (Acid side)	Limiting pH (Alkali side)
0.923	1.65	11.1
0.738	1.75	10.8
0.369	2.56	10.4
0.184	3.40	9.4
0.074	4.31	8.0

The ranges of gel formation for the two sodium silicate solutions, have been represented in Fig. 1, where the concentrations of the silicate solutions, expressed in terms of mols SiO_2 per litre, have been plotted against the limiting pH values. The curve for the sodium silicate solution in which the ratio of $Na_2O:SiO_2$ was as 1:2.25 has also been included for comparison.

The investigations of Herman[1] and the viscosity measurements of Main[2] seem to show that as the molecular proportion of SiO_2 in the sodium silicates increases, the amounts of silica present in a colloidal form also increases. It was therefore expected that by using sodium silicate solutions containing gradually increasing proportions of silica, the range of pH values within which silica gels are formed would change appreciably. From Fig. 1, however, it is seen that the curves for all the three sodium silicate solutions have the same shape and differ very little from one another. The ranges for the pH values on the alkali sides of the curve are practically coincident, whereas on the acid side the range widens slightly, though quite uniformly, as the molecular proportion of silica in the silicates increases. It is evident, therefore, that the presence of a certain amount of silica in a colloidal form in the sodium silicate solutions does not appreciably alter the limiting ranges of hydrogen ion concentrations as determined in these experiments.

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[1] J. Phys. Chem., 31, 355 (1927).

[2] J. Phys. Chem., 30, 535 (1926).

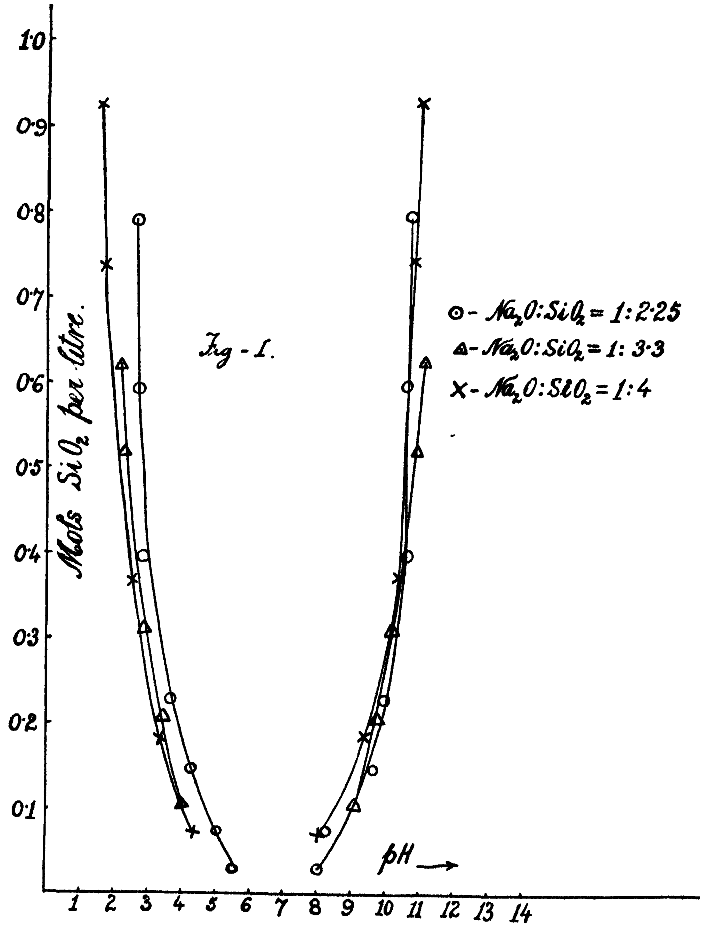

FIG. 1

In the previous paper, the formation of silica gels by the action of ferric chloride on sodium silicate solutions was also studied, and from the results of our experiments it was suggested that when ferric chloride was added to a sodium silicate solution ferric silicate was formed in the first instance. During the course of the present investigation, an attempt has been made to obtain further experimental support for the above view.

Solutions of the alkali silicates can be titrated quite consistently against ferric chloride solutions by using potassium ferrocyanide as the indicator.

The end point, which is indicated by the appearance of green colour, is quite sharp, and the titration values obtained are quite concordant. It is necessary, however, to carry out the titrations in sufficiently dilute solutions in order to avoid the formation of a gel. A solution of potassium metasilicate and solutions of sodium silicates, containing Na_2O and SiO_2 in the ratios of 1:2.25, 1:3.3 and 1:4 respectively, were made exactly equivalent with respect to a $N/_2$-solution of hydrochloric acid. They were then titrated against a standard ferric chloride solution and gave the following results:

TABLE III

	Gram-mols K_2O or Na_2O per litre	Gram-mols SiO_2 per litre	Ratio SiO_2 Na_2O or K_2O	Volume of M/5-ferric chloride per 10 c.c. of silicate sol
Potassium meta-silicate	0.415	0.415	1	15.15 c.c.
sodium silicate	0.415	0.934	2.25	14.65 c.c.
sodium silicate	0.415	1.37	3.30	14.0 c.c.
sodium silicate	0.415	1.66	4	13.65 c.c.

From the above values, it is clear that the volumes of a M/5-ferric chloride solution, required to react completely with 10 c.c. of sodium silicate solutions of different ratios but of equivalent alkali content, are all within 10 per cent. of one another. Evidently, therefore, the reaction depends mainly on the alkali content of the solution, rather than the amount of silica it may contain, suggesting that ferric hydroxide is formed in each case. As all the silicate solutions contained the same amounts of Na_2O (or K_2O), the amounts of ferric chloride required for titration should be the same if all the added ferric chloride were to be converted mainly into ferric hydroxide. On the other hand, the fact that the amounts of ferric chloride solution required for titration with the various silicate solutions, do not vary from one another by more than 10 per cent., does not in any way disprove the possibility of the formation of ferric silicate, because a greater silica content does not necessarily mean that a greater amount of silicate ions is present. If the excess of silica in the 1:3.3 and 1:4 ratio silicate solutions be present either in the form of complex silicate ions or as colloidal aggregates, the sodium silicate solutions might titrate with the same amounts of ferric chloride.

In order to elucidate the above point, a series of measurements of the amounts of heat developed during the reaction between a standard ferric chloride solution and the alkali silicate solutions have been carried out. The heat measurements were performed in a seamless silver calorimeter which was kept suspended in a long Dewar cylinder by means of fine silk threads. An arrangement was set up for stirring the solutions at a uniform rate, and the temperatures were read by means of a Beckmann thermometer. The heat capacities of the calorimeter together with its contents were carefully determined in each case separately after each heat measurement.

A series of dilute solutions of the alkali silicates equivalent in terms of Na_2O (or K_2O), were prepared and were titrated against a standard dilute ferric chloride solution. Measured volumes of the silicate solutions and the requisite amount of ferric chloride solution were allowed to react in the calorimeter with uniform stirring. The ferric chloride solution was also placed inside the Dewar vessel so that it attained the right temperature before it was mixed with the silicate solution. The amounts of heat developed when one gram mol of ferric chloride has been completely reacted upon by alkali silicate solutions are given below:

TABLE IV

Showing the amount of heat developed per gram mol of ferric chloride reacted upon

Silicate solution	Molar ratio Na_2O (or K_2O)/SiO_2	Amount of heat
Potassium meta-silicate	1:1	20036 calories
Sodium silicate	1:2.25	11051 "
Sodium silicate	1:3.3	8164 "
Sodium silicate	1:4	6629 "

From Table IV, it will be seen that as the ratio of SiO_2 in the silicate solutions increases, the amounts of heat, per gram mol of ferric chloride reacted, decreases very markedly. The amount of heat developed when one gram mol of ferric chloride is acted upon by sodium hydroxide is 25530 calories, which is distinctly greater than any of the amounts of heat developed during the present measurements. The amount of heat developed in the case of potassium metasilicate is 20036 calories, which, after allowance is made for the difference between the heats of formation of potassium chloride and sodium chloride, is about 25 per cent less than the amount of heat developed when one gram mol of ferric chloride is converted into ferric hydroxide. In the case of the other sodium silicate solutions the difference is still greater. Thus, so far as these experiments go, it seems unlikely that ferric hydroxide is the main product of the reaction between ferric chloride and the alkali silicates.

As a result of a series of investigations on the sodium silicate solutions, Herman[1] has come to the conclusion that only two compounds are indicated as stable in solution, namely, $Na_2O.SiO_2$ and $Na_2O.2SiO_2$; the 1:3 and 1:4 ratio silicate solutions are not definite salts but consist of complex aggregates or ionic micelle in concentrated solutions. From the heat measurements, it is found that the amounts of heat developed decrease in about the same proportion in which the molar ratio of SiO_2 in the silicates increases. If the above view of Herman be taken as a true representation of the constitution of the silicates, the simplest explanation for the values, obtained from the heat measurements, appears to be that as the molar ratio of SiO_2 in the silicate solutions increases in an arithmetic progression, the rate of formation of the complex aggregate or ionic micelle increases in a geometric progression.

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[1] J. Phys. Chem., 31, 355, 511 (1927).

It may be pointed out, however, that as the ratio SiO_2/Na_2O (or K_2O) increases from 1 to 4, the heat of reaction with ferric chloride decreases regularly. If the reaction product was entirely ferric hydroxide in every case, the heats of reaction would have been more or less the same and fairly close to the heat of reaction between ferric chloride and sodium hydroxide. If, on the other hand, all the alkali silicate solutions contained only one or two simple silicates with aggregates of colloidal silica in the case of the higher ratio silicates, it might be expected that the heat of reaction would attain a constant value after a certain stage. The regular decrease in the heats of reaction, taken in conjunction with the titration results given in Table III, appears to point to the formation of complex silicate ions with increase of silica in the molecule. Herman[1] has determined the transport number of the silicate ion in aqueous alkali silicate solutions. In ratios 1:2, 1:3 and 1:4, the transport number of the silicate ion is high, and the silicate anion contains more than one SiO_2 per divalent charge; the average number of mols SiO_2 per divalent charge being equal to the ratio. In ratios 1:2, 1:3 and 1:4 the anion is not simple SiO_3 ion but may be definite complex silicate ion. Schwarz and Menner (loc. cit.) claim the existence of at least seven silicic acids or hydrates of SiO_2, although our knowledge of these is only very slight. Considering, however, the fact that the sodium silicate solutions, which are equivalent in terms of Na_2O, react with practically the same amounts of a ferric chloride solution, it would appear that there are more than one kind of ferric silicate, each having a different heat of formation. In the absence of further experimental data it is, however, not possible to come to any definite conclusion.

Summary

1. The optimum conditions for the formation of silica gel by the action of hydrochloric acid on sodium silicate solutions of 1:3.3 and 1:4 ratios have been studied; the limiting ranges of pH values, in which gel formation takes place, have been accurately determined.

2. The presence of a large amount of silica in the higher ratio sodium silicate solutions, either in the form of colloidal aggregates or as definite complex silicate ions, does not appreciably affect the conditions of gel formation.

3. Ferric chloride solutions can be titrated against sodium silicate solutions with the help of potassium ferrocyanide as an indicator.

4. The amounts of heat developed when one gram mol of ferric chloride is acted upon by sodium silicate solutions of different ratios have been determined.

5. The heat of reaction decreases in a regular manner with increase in the ratio SiO_2/Na_2O (or K_2O) from 1 to 2 to 3 to 4.

6. The heat measurements lend support to the view that the reaction between ferric chloride and the sodium silicate solution results mainly in the formation of ferric silicates.

Chemical Laboratory,
Science College, Patna.
June, 1930.

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[1] J. Phys. Chem., **30**, 359 (1926).

THE DETERMINATION OF THE HYDROGEN ION CONCENTRATION IN GOLD SOLS

BY T. R. BOLAM AND J. CROWE

Introduction

Despite the large amount of research which has been carried out on gold sols, considerable uncertainty exists regarding the use of the hydrogen electrode for the determination of the hydrogen ion concentration in these systems. Herstad,[1] who appears to have been the first to apply the method, states that by careful working reliable results could be obtained. Actually his pH values are uncertain by at least ±0.5 pH. The next reference to the subject is to be found in a paper by Kautzky and Pauli,[2] who reported that it was impossible to obtain a steady potential with red gold sols and that the latter were coagulated by the hydrogen. These conclusions were based on an investigation by Adolf and Pauli,[3] an account of which appeared in the following year. Dialysed sols, prepared by Zsigmondy's method, were the object of study and the hydrogen electrode was found to be extremely sensitive to either dissolved or colloidal gold. To quote from the paper itself, "Diese Veränderung der Elektrode tritt schon bei so geringen Goldspuren ein, dass sie unter Umständen jedem feinen analytischen Goldnachweis gleichkommen oder sogar überlegen sein kann". No difficulty was encountered in measuring the hydrogen ion concentration in ordinary solutions of potassium or barium chloride, or in the solution ("Flockungsfiltrat") obtained by coagulating a sol with a sufficiently large amount of these salts and removing the gold by filtration. In the latter case the hydrogen ion concentration was found to be about 1×10^{-5} N. The experience of Tartar and Lorah[4] was the same as that of Adolf and Pauli. These workers were investigating the influence of pH (over the range 2-9) on the protective action of gelatine on Zsigmondy sols and found that the hydrogen electrode gave erratic results unless the gold was carefully eliminated. The gelatine itself did not cause variations greater than 0.2 millivolt. Wo. Ostwald[5] also reports that he encountered the same difficulties as Pauli and Adolf.

Beaver and Müller in a paper[6] describing a very careful study of the action of ultraviolet light on various gold sols make the following statement. "Electrometric titrations of the chloroauric acid with 0.1 N potassium carbonate were therefore made at room temperature (22-25°). A curve was then plotted of c.c. of potassium carbonate against pH of the solution for the given gold content, and from this curve solutions of definite pH were made, heated to 65° and reduced." There is no mention of any difficulty with the hydrogen electrode due to the presence of gold in the solution. In one series of experiments the pH varied from 3-10 approximately. The latest work involving the use of the electrode in gold sols is that of Reinders and Bendien.[7] In this case the sols were prepared by Bredig's method, and gelatine and casein were added to them. Here again there is no suggestion that the E.M.F. measurements were troublesome.

The following is an account of an investigation undertaken to ascertain whether it is possible to define conditions which permit of the accurate determination of the hydrogen ion concentration in gold sols by means of the hydrogen electrode.

Apparatus

Some difficulty was experienced in finding a suitable form of hydrogen cell. The apparatus shown in Fig. 1 was finally devised and found to be satisfactory. A is the hydrogen electrode, B is a saturated potassium chloride calomel half-cell, and C a bridge of saturated KCl. By opening the tap D the pressure is released when the rubber stoppers E and E′ are inserted in the U-tube. Taps F and G are opened only when a reading is actually being made, D being then closed. A spiral of platinised platinum or gold wire was found to give better results than a sheet of platinised platinum as the electrode itself. The hydrogen is introduced at the lower end of the spiral by means of a narrow turned-up glass tube H. A stream of fine bubbles is thus formed which fills the inside of the spiral and passes out between the coils. In this way rapid equilibrium is established between the electrode and the sol or solution to be investigated. I is a glass cap, and J a rubber ring holding the electrode in position. The advantages of this form of apparatus are:

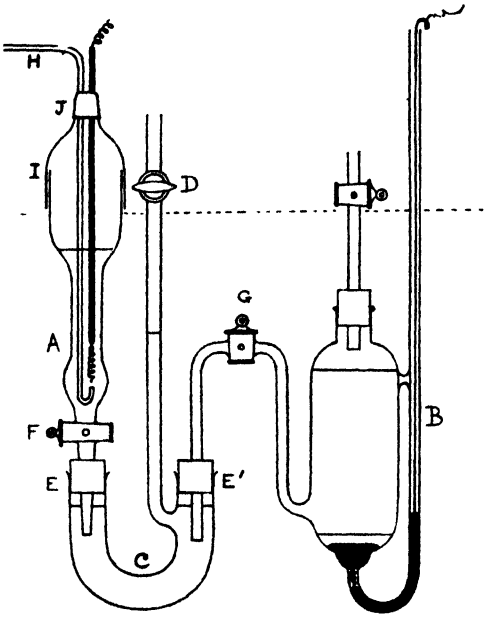

FIG. 1

(1) Only 3 or 4 c.c. of sol are necessary for a determination.

(2) The column of poorly conducting liquid between the electrode and the saturated KCl is very short. A high resistance is thus avoided and the null point can be accurately determined.

(3) The hydrogen electrode attains equilibrium rapidly.

(4) The simple form of the apparatus permits of quick and thorough cleansing.

(5) The cell can be immersed in a thermostat.

The hydrogen was generated from zinc and hydrochloric acid and purified by passing through (1) conc. KOH, (2) alkaline $KMnO_4$, (3) neutral $KMnO_4$, (4) distilled water, (5) sol (or solution). The E.M.F. values were obtained by the usual compensation method, the instruments employed being such that individual determinations were accurate to 0.1 millivolt. All experiments were carried out at 20° C, the cell being immersed in a glass-walled thermostat up to the level indicated in Fig. 1. Two saturated calomel electrodes (S.E.) were used as working electrodes and checked by comparison with two N/10 calomel electrodes (D.E.). All four were prepared from carefully purified mercury, electrolytic calomel, and Kahlbaum KCl. The E.M.F. of the combination, Hg, Hg_2Cl_2, satd. KCl, N/10 KCl, Hg_2Cl_2, Hg was found to be 0.0886 volt, with both sets of electrodes, so that taking 0.3379 volt as the standard electrode potential of the D.E.[8] at 20°C., that of the S.E. was equal to 0.2493 volt. Clark[8] gives 0.2492 volt. A test was made of the hydrogen electrode with three of Sörensen's standard phosphate mixtures (pH = 5.91, 6.47, 6.81 respectively).[8] The electrode rapidly attained equilibrium and gave very steady and reproducible potentials, the derived pH values differing from Sörensen's by not more than 0.01.

Zsigmondy and Nordenson Sols

Repeated trials showed that it was impossible to obtain a constant E.M.F. with a sol* prepared by Zsigmondy's method (reduction by formaldehyde of gold chloride made alkaline with potassium carbonate). There was a continuous increase in the E.M.F., which amounted to about 30 millivolts in the first two hours. In no case however could any sign of coagulation of the sol during an experiment, or even hours after, be detected. A pronounced drift in the same direction also took place with the liquid obtained by precipitating the gold with potassium chloride and removing the precipitate by filtration.

In contrast with the Zsigmondy sols, those prepared by Nordenson's method gave very satisfactory results. The principle of the method is the reduction of gold chloride by hydrogen peroxide under the influence of ultra-violet radiation. In the present instance a small quantity of potassium carbonate was added, which, while insufficient to give a neutral or alkaline sol, was found to increase the degree of dispersion. Table I contains the data for the sol prepared from 2.0 c.c. of 0.6% $HAuCl_4$, $4H_2O$ (Merck) in 125.0 c.c. conductivity water + 0.6 c.c. of 0.2 N K_2CO_3 (Kahlbaum) + 0.4 c.c. Perhydrol (Merck), which is quite representative. A separately prepared sample of the sol was used for each experiment.

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*All the sols used in this investigation, whatever the method of preparation, were bright red in colour, showed no sign of opalescence, and proved to be very stable. Further details of preparation, etc., will appear in a subsequent communication.

TABLE I

Nordenson Sol

Preparation	Time (mins.)	E.M.F. (volts)	pH
1.	19	0.4772	3.92
	32	0.4774	3.92
	52	0.4793	3.96
	74	0.4799	3.97
	122	0.4802	”
2.	25	0.4777	3.93
	45	0.4777	”
	65	0.4779	”
	90	0.4766	3.91
3.	30	0.4779	3.93
	52	”	”
	171	”	”

It was thought that if the Zsigmondy sols were buffered by the addition of small quantities of suitable electrolytes it might be possible to get steady E.M.F. values. Accordingly 20 c.c. Zsigmondy sol (2.0 c.c. 0.6% gold chloride in 120 c.c. water + 3.0 c.c. 0.2 N K_2CO_3 + 3.0 c.c. 0.4% formaldehyde (specially prepared) were mixed with 1.0 c.c. M/15 Na_2HPO_4(A.R.) + 1.0 c.c. M/15 KH_2PO_4 (A.R.), and three portions of the mixture tried. The results are given in Table II.

TABLE II

Zsigmondy Sol + Phosphate Buffer

	Expt. I		Expt. II		Expt. III	
Time (mins.)	E.M.F. (volts)	pH	E.M.F. (volts)	pH	E.M.F (volts)	pH
10	0.6620	7.10	0.6637	7.12	0.6642	7.13
20	0.6630	7.11	0.6648	7.14	0.6652	7.15
30	0.6633	7.12	0.6650	7.15	”	”
60	”	”	”	”	”	”
84	”	”	”	”	”	”

It would appear that the change in E.M.F. observed with the original Zsigmondy sol was not due to any deleterious action of the gold upon the electrode but to the absence of equilibrium between the solution and the hydrogen, i.e. to change in the hydrogen ion concentration. There is every reason to believe that the relatively high concentration of potassium carbonate used in the preparation of these sols is the source of disturbance. In dilute unbuffered alkaline solutions (the above Zsigmondy sol had pH = 9 approx.) the participation of any CO_2 present in the acid-base equilibrium is of great importance.[8] We may therefore attribute the E.M.F. drift in Zsigmondy sols to the removal of CO_2 by the hydrogen stream.

Experiments with "Citrate" Gold Sols

If the above explanation is correct no difficulty should be experienced in obtaining a steady and reproducible potential in sols prepared by replacing potassium carbonate in the Zsigmondy procedure by tri-sodium citrate. Table III gives the results in the case of a "citrate" sol containing 0.31 millimols per litre of sodium citrate. Two quite separate preparations were examined.

TABLE III

"Citrate" Sol

Preparation	Time (mins.)	E.M.F. (volts)	pH
1. Sample (a)	15	0.5461	5.11
	30	"	"
	42	"	"
" (b)	12	0.5469	5.12
	25	"	"
	40	"	"
2.	12	0.5458	5.10
	23	0.5463	5.11
	33	0.5461	"

Variation of E.M.F. with Composition of Sol

Three series of sols were prepared by reduction with formaldehyde in the absence of potassium carbonate, the first containing increasing amounts of sodium citrate, the second, of disodium hydrogen phosphate, and the third, of sodium hydroxide (from the metal). In every case the reduction mixture contained 1.0 c.c. 0.6% gold chloride (diluted with sufficient water to give final volume of 128 c.c.) + 0.4 c.c. M sodium citrate 10/($C_6H_5O_7Na_2$. 5½ H_2O

TABLE IV

"Citrate" Sols

Final concn. of Sodium Citrate (millimols/litre)	Concn. of Na (milligrm.-equivs./litre)	E.M.F. (volts)	pH
0.31	0.93	0.5461	5.11
0.35	1.05	0.5553	5.27
0.57	1.71	0.5801	5.69
0.64	1.92	0.5857	5.79
0.71	2.13	0.5923	5.90
0.78	2.34	0.5982	5.95
0.85	2.55	0.5989	6.02
1.06	3.18	0.6063	6.14
1.42	4.26	0.6165	6.32
1.80	5.40	0.6236	6.44
2.13	6.39	0.6274	6.51

TABLE V

"Phosphate" Sols

Final concn. of Na_2HPO_4 (millimols/litre)	*Concn. of Na (milligrm.-equivs./litre)	E.M.F. (volts)	pH
0.08	1.09	0.5578	5.31
0.16	1.25	0.5722	5.56
0.31	1.55	0.5927	5.91
0.78	2.49	0.6295	6.54
1.17	3.27	0.6497	6.89
1.56	4.05	0.6623	6.11
2.34	7.28	0.6722	7.28
2.73	7.36	0.6767	7.36
3.52	7.42	0.6806	7.42

TABLE VI

"Hydroxide" Sols

Final concn. of NaOH (millimols/litre)	*Concn. of Na (milligrm.-equivs./litre)	E.M.F. (volt)	pH
0.0780	1.008	0.5611	5.37
0.156	1.086	0.5787	5.67
0.31	1.24	0.5961	5.97
0.47	1.40	0.6194	6.37
0.62	1.55	0.6428	6.78
1.56	2.49	†(0.777 ±)	(9.1 ±)
3.12	4.05	†(0.895 ±)	(1122 ±)

*0.31 × 10^{-3} M sodium citrate present in every case.

†In the case of these preparations there was a drift in the E.M.F. The initial values are, however included to indicate the order of magnitude of the pH.

by Kahlbaum). To this was added the appropriate quantity of citrate, phosphate, or hydroxide and then, after heating, 3.0 c.c. 0.4% formaldehyde. E.M.F. determinations were made on two separate portions of each sol and the mean values are given in Tables IV, V, and VI. With the exception of the last two preparations in Table VI, the E. M. F.'s were very constant and reproducible. Duplicates agreed generally to 0.1 millivolt, and were never farther apart than 0.5 millivolt.

If the curves showing the variation of the pH with concentration of sodium are drawn (Fig. 2.) it will be seen that they occupy positions to be expected from a consideration of the relative degrees of alkalinity of sodium hydroxide, phosphate and citrate. This affords strong evidence that the potential of the hydrogen electrode in these sols depends in the normal manner upon the activity of the hydrogen ion.

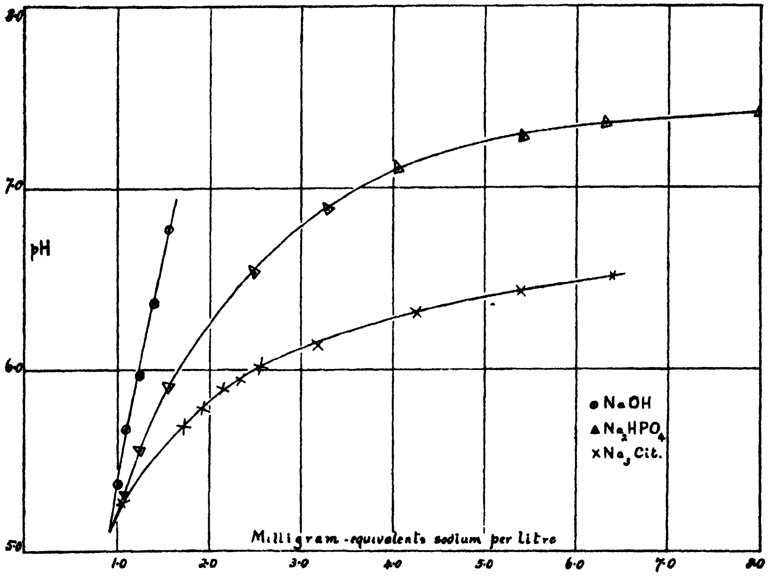

FIG. 2

Morton[9] in the course of a very accurate electrometric titration of 0.01 M citric acid with 0.01 M sodium hydroxide found that when the ratio $\frac{\text{moles base}}{\text{moles acid}}$ was equal to 2.769, the pH was 6.405, the concentration of citrate in the mixture being 2.65×10^{-3} M. Extrapolating the data in Table IV to this concentration of citrate we find that the corresponding pH is about 6.60. In calculating the base/acid ratio for comparison with Morton's figure, account must be taken of the acid produced during the reduction of the gold chloride. Assuming that the reduction is complete and wholly due to the formaldehyde, then according to Vanino and Hartl[10] the liberation of 2 atoms of gold requires 11 molecules of NaOH. In the present case this means that 0.626×10^{-3} moles per litre of base are neutralised by hydrochloric and formic acid. We therefore have for the citrate equilibrium, $\frac{\text{moles base}}{\text{moles acid}} = \frac{(3 \times 2.65) - 0.626}{2.65} = 2.764$, i.e. almost identical with Morton's value. The difference of 0.20 between the pH values is probably connected with the fact that the citrate itself acts as a reducing agent, but the information necessary to make allowance for this is lacking at present.

It should be emphasised that in none of these experiments could there be detected the slightest tendency on the part of the gold to coagulate in the hydrogen cell. Moreover if an electrode was placed in a standard solution immediately after use in a gold sol it invariably acquired the correct potential within 20 minutes. If the gold exerted any ill effect upon the electrode it was certainly of a very transitory nature.

Conclusions

The results of this work establish beyond reasonable doubt that under circumstances the hydrogen electrode may be relied upon as a means of determining the hydrogen ion concentration in a gold sol. It has been shown that, as would be predicted from the behaviour of ordinary unbuffered solutions, the sol must be either sufficiently acid or suitably buffered in order to secure steady and reproducible potentials.

The unsatisfactory working of the electrode observed by Adolf and Pauli[3] and Tartar and Lorah[4] can hardly be due to the absence of the above conditions. The dialysed sols studied by Adolf and Pauli contained about 1×10^{-5} N hydrogen ion, and gelatine, which exerts a buffering action, was present in the sols of Tartar and Lorah. Moreover both pairs of workers report that, provided all the gold was removed, no difficulty arose in the use of the hydrogen electrode.

As far as the available information goes, the essential difference between the sols employed by these investigators and those examined in the experiments here described, appears to be that the former contained complex organic substances. Adolf and Pauli dialysed their sols by means of parchment paper membranes and the work of Wintgen[11] and of Thiessen and Heumann[12] has shown that appreciable quantities of some protective colloid passes into the sol from such membranes. Wintgen and his co-workers found that this substance could be present in the sol to the extent of 50% of the weight of the gold, and Thiessen that it was not eliminated by prolonged use and washing of the membranes. Gelatine of course was present in the sols of Tartar and Lorah. It may be tentatively suggested that the hydrogen electrode gave erratic results owing to some combined action of the gold and the foreign material. The sols investigated by Reinders and Bendien[7] also contained gelatine but unfortunately these workers give no description of their E.M.F. measurements.

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References

[1] Herstad: Kolloidchem. Beihefte, **8**, 409 (1916).
[2] Kautzky and Pauli: Kolloidchem. Beihefte, **17** 303 (1923).
[3] Adolf and Pauli: Kolloid-Z., **34**, 30 (1924).
[4] Tartar and Lorah: J. Phys. Chem., **29**, 794 (1925).
[5] Ostwald: Kolloid-Z., **40**, 204 (1926).
[6] Beaver and Müller: J. Am. Chem. Soc., **50**, 308 (1928).
[7] Reinders and Bendien: Rec. Trav. chim., **47**, 978 (1928).
[8] Clark: "Determination of Hydrogen Ions", pp. 285, 456, 114, 267-9 (1923).
[9] Morton: Trans. Faraday Soc., **24**, 14 (1928).
[10] Vanino and Hartl: Kolloid-Z., **1**, 272 (1907).
[11] Wintgen: Kolloid-Z., **40**, 301 (1926).
[12] Thiessen and Heumann: Z. anorg. Chem., **148**, 387 (1925).

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ENTROPY, ELASTIC STRAIN, AND THE SECOND LAW OF THERMODYNAMICS; THE PRINCIPLES OF LEAST WORK AND OF MAXIMUM PROBABILITY

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The purpose of this paper is to point out a new mechanical aspect of entropy with special reference to simple fully excited gas. By relying on the geometrical expression for weight, $W = N^N (r_1 \ldots r_N)$ and taking strains to include unit extensions in velocity and momentum space as well as ordinary space, a relation is established between entropy and the total strain: $S = kY$; $Y = \log W$, where S is the entropy, k is Boltzmann's constant, Y the total strain, and W is the a-priori probability. The Lagrange multiplier method is applied to statically indeterminate frames as well as gas theory, and both cases show that the Principle of Least Work, or Internal Energy is equivalent to the Principle of Maximum Entropy, Strain and a-priori probability. Furthermore the equations which by the Lagrange method determine the equilibrium state are shown to represent balance between true stress and strain both in gas theory and in the statics of indeterminate frames, revealing the operation in these two domains of the same identical principles (not an analogy). And the modulus of elasticity for these stresses and strains acting in momentum space is the ordinary bulk modulus p (the pressure) that also applies to volume expansions in ordinary space. Then the second law of thermodynamics and the automatic increases of entropy that it represents are explained as due to increased strain (in momentum space as well as ordinary space) under action of corresponding stresses, rather than as in statistics by the unsatisfactory ergodic hypothesis.

Altho these ideas are radical in that the statistical aspect is purposely put aside in favor of the geometrical and mechanical aspect, yet they have classical support from Boltzmann's H-theorem which shows by the method of collisions (and the forces involved) that the rate of change of entropy is positive. On the other hand Boltzmann's H-theorem implying the operation of *forces* to bring about the increase of entropy towards equilibrium, is in disagreement with any statistical theory that requires equilibrium to be reached *without* operation of forces, solely from probability considerations and the ergodic hypotheses.

It seems very possible that equilibrium between stresses and strains may accompany and account for various other phenomenon of gaseous equilibrium such as fluctuations and Brownian motion that usually are treated by the statistical method, and are not within the scope of the present article. Since the geometrical weight method has already been applied to the new quantum statistics,[1] it seems likely that the present mechanical stress-strain theory that comes from the geometrical weight method, can also be extended to include the new statistics.

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[1] Chandrasekhar: Phil. Mag., 9, 621 (1930).

1. The Geometrical Expression for Weight and the Statistical Expression for Weight

The familiar expression for weight used in statistical mechanics is:

$$W = \frac{N!}{n_1!n_2! \dots n_k!} (\omega_1)^{n_1} (\omega_2)^{n_2} \dots (\omega_k)^{n_k} \tag{1}$$

where the ω's are small volumes in "μ-space" (of 6 to 12 dimensions according as we refer to molecules with three or six degrees of freedom). And their product (when each is raised to the indicated power) gives the elementary volume in so called γ-space, which is known as the geometrical part of the weight given by (1). The numerical coefficient involving the factorials of the n's is the statistical part and indicates the number of distinct arrangements in this γ-space.

This expression for weight (1) has been shown[1] to be equivalent to the geometrical expression for weight. To see this consider one dimension of velocity or momentum space, then each ω will refer to a velocity or momentum range including the corresponding n molecules, which we can refer to as s. If we use the approximation:

$$\log N! = N \log N - N \tag{2}$$

then the statistical part of (1) is readily seen to be equivalent to $N^N / (n_1^{n_1} n_2^{n_2} \dots n_k^{n_k})$ so that (1) may be written:

$$W = \frac{N^N}{n_1^{n_1} n_2^{n_2} \dots n_k^{n_k}} (s_1)^{n_1} (s_2)^{n_2} \dots (s_k)^{n_k} \tag{3}$$

which refers to one dimension say of velocity space. Now it is noteworthy in connection with this theory that the ω's (and hence the s's) are arbitrary, (except that in the quantum theory they determine energy levels and are integral multiples of h) and it is in connection with this fact that the geometrical treatment differs from the statistical one, for the prevailing mode is to choose the ω's as all equal (or at least constant), and then one can readily employ the familiar method used by Boltzmann of maximizing W thru variation of the n's, keeping the total energy constant, and thereby derive the Maxwell Boltzmann distribution law. It is equally permissible, however, to keep the n's constant and let the ω's which are the geometrical part of (1) vary, instead of Boltzmann's method of keeping the ω's constant and varying the n's, i.e. the statistical part. And in particular we may take each n equal to unity, thereby removing the statistical aspect entirely and then if we refer to (3) instead of (1), the s's which correspond to the ω's will be the range[2] in velocity space corresponding to separate molecules:

$$r_i = \frac{1}{Nf(u_i)} = u_{i+1} - u_i \tag{4}$$

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[1] Kimball: J. Phys. Chem., 33, 1558 (1929).

[2] Kimball: loc. cit.

And these r's are the velocity differences between successive molecules in velocity space used in deriving the geometrical expression for weight:

$$W = N^N(r_1 r_2 \ldots . r_N) \tag{5}$$

Thus it is readily seen that (3) reduces to (5) when we take $s_i = r_i$ and $n_1 = n_2 = n_3 \ldots . n_k = 1$. The expression (5) is geometrical because the variable, vital part is the geometrical velocity (or action) range that includes each particle. On the other hand, the variable, vital part of (1) and (3) is statistical being the n's, necessarily integers associated with arbitrary constant compartments of μ-space.

2. Entropy, Strain, Weight, A-Priori Probability and the Third Law of Thermodynamics

If we interpret the r's given by (4) as momentum ranges instead of velocity ranges, then the weight that measures the thermodynamic probability, taking account of ordinary space ranges as well as three dimensions in momentum space, is given by:

$$W = N^{3N}(r_1 r_2 \ldots . r_N)^3 V^N = (Nr)^{3N} V^N \tag{6}$$

where the right member gives the weight in the terms of the range r of a molecule in its mean energy state corresponding to the temperature in question. (See eqs. (32) and (39) of Entropy and Probability).[1] When (6) is substituted in Boltzmann's equation we have the known expression for entropy of monatomic gas,

$$S = k\log W + C = R\log V(2\pi emkT)^{3/2} + C = R\log VN^3 + 3k\Sigma\log r_i + C \tag{7}$$

and hence:

$$dS = R\frac{dV}{V} + 3k\Sigma\frac{dr_i}{r_i} = R\frac{dV}{V} + 3R\frac{dr}{r} \tag{8}$$

Equation (8) shows that the change in Entropy equals k times the sum of the corresponding strains for the separate molecules, both in ordinary space and in momentum space. Entropy thus appears as an extensive physical quantity, being k times the integral of the strains plus a constant, i.e., it is k times the total strain, and the constant of integration gives the lower boundary from which strain is to be measured. Thus if we let Y represent the total strain or yielding of the gas, we have:

$$S = kY;\ Y = \log W;\ W = e^Y \tag{9}$$

The concept weight is introduced into physics to avoid the indeterminate aspects of thermodynamic probability which should be a proper fraction, whereas the denominator to be used is unknown. Eq. (9) shows how this weight that measures the a-priori probability of a gaseous state is related to the strain. This gives additional physical significance to the idea of weight, heretofore known mainly as the volume in so called γ-space, and perhaps pushes thermodynamic probability further into the background. We show below how the state of maximum probability corresponds to the equilibrium equations between stress and strain, and represents by (9) a state of maximum strain. It is like the statics of indeterminate frames (see below) where the equilibrium equations correspond to a state of maximum strain for given internal energy. That is to say, the gas yields as much as it can, subject to the boundary conditions on its volume and energy.

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[1] Kimball: Loc. cit.

Altho these results are derived from considerations of monatomic gas obeying the gas law, they are readily seen to apply to complex gases having more than three degrees of freedom, since these gases also have their entropies expressible in terms of momentum and action range, according to Entropy and Probability,[1] equation (48), which form gives the dS like (8) as the sum of the strains. The present treatment suggests that perhaps any probability theory available to calculate entropy according to Boltzmann's equation (6) (or statistical theory resting on probability) has value by virtue of its relation to the forces and balancing strains, for mechanical strain appears to be the corner stone of *a-priori* probability wherever (9) can be applied to gases and other branches of physics.

It is to be emphasized that (9) refers *only* to *a-priori* probability. It is clear that there are other types of probability which are not based on the probability axioms and which are not related to entropy and mechanical strain according to (9). Thus the usual probability expression associated with the Maxwell distribution law, $dN/N = f(u)\,du$, is du times the reciprocal of the weight per molecule, $w = Nr = 1/f(u)$. It is this latter (Type A probability) which is based on the probability axioms and is related to entropy and strain according to (9). On the other hand $f(u)\,du$ can not be used in (7) or (9) to give entropy and strain, and thus represents a type of probability (Type C) to which Boltzmann's equation does not apply. (See Entropy and Probability,[1] 4, eqs. (15) and (25)).

When entropy is clearly related to probability according to Boltzmann's relation, no case appears where it has been shown that these are not related to mechanical strain according to (9). The present paper shows how (9) applies in ordinary gas theory, and likewise it is planned to show how it applies to fluctuations in gas where equilibrium prevails. The applicability of (9) to electronics, the Schott effect and other cases remains to be proved or disproved.

If (9) holds true all the way down to absolute zero, the corresponding interpretation of the third law of thermodynamics is that the total strain of crystalline substances at the absolute zero is zero.

If entropy is proportional to strain, it suggests that the equilibrium state of maximum entropy and strain is brought about thru the action of stresses. To prove this we note how forces may act in velocity and momentum space, first, however taking note how the principle of maximum entropy, probability and strain is related to the principle of minimum internal energy.

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[1] Kimball: Loc. cit.

3. The Principle of Maximum Entropy, Probability and Strain is Equivalent to the Principle of Least Work or Internal Energy

It is well known that equilibrium conditions in gas theory correspond to the state of maximum entropy and probability. If we restrict attention to one dimension of velocity space, the probability is given by (5) above.

The Maxwell distribution law of velocities is obtained by maximizing the probability (5) subject to the condition that the energy remain constant. Using the Lagrange method of multipliers we form the function:

$$F = W + \lambda U \tag{10}$$

where U the energy is a homogeneous quadratic function of the velocity coordinates, and take the partial derivatives of (10).

$$\frac{\partial F}{\partial u_i} = \frac{-Wd}{du_i}(\log f(u_i)) + \lambda m u_i = \frac{Wd}{du_i}(\log r_i) + \lambda m u_i = 0 \tag{11}$$

Equations (11) are of the same form as if W were kept constant and U were being minimized. Thus we see that these equations (11), and the Maxwell distribution law arising from them, represent the state of minimum internal energy for a given constant probability (or entropy) as well as the state of maximum probability for a given constant internal energy.

Altho (11) are merely conditions for the extremal values of W or U subject to the constancy of the other, it is readily shown by taking the second partials of U subject to the constant W condition that these partial derivatives are positive and satisfy the sufficiency condition to make U a minimum rather than a maximum.

The equivalence of these two principles also holds in the domain of elasticity theory as applied to engineering problems. Thus the problem used in Church's "Mechanics of Internal Work"[1] to illustrate Castigliano's Principle of Least Work, may be treated by the Lagrange method for conditional maxima and minima. The extension of a bar in the frame is given in terms of the tension by:

$$y = CT;\ \text{and}\ C = L/EA \tag{12}$$

and L is the length, E the elastic modulus, and A the cross section of the ba and the internal energy is given by:

$$U = \tfrac{1}{2}(C_1T_1^2 + \ldots . + C_6T_6^2) \tag{13}$$

Then if P is the load, we have from statics: (see figure1)

$$P = T_1 + \frac{T_3}{\sqrt{2}} + \frac{T_6}{\sqrt{2}};\ Q = T_3 - T_6 = O;\ R = T_1 + \frac{T_4}{\sqrt{2}} + \frac{T_5}{\sqrt{2}} = O;\ S = T_4 - T_5 = O$$

$$\frac{P}{2} = T_1 - T_2. \tag{14}$$

where Q, R and S are convenient notations for the indicated zero value constants of elementary statics. We take these as five conditions on the T's and form the function:

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[1] I. P. Church: "Mechanics of Internal Work."

$$F = U + \lambda P + \mu Q + \nu R + \xi S + \rho \frac{P}{2} \tag{15}$$

where the Greek letters are undetermined constants. Now take the partial derivatives for the six independent variables:

$$\begin{aligned}
\frac{\partial F}{\partial T_1} &= C_1T_1 + \lambda + 0 + \nu + 0 + \rho = 0 \\
\frac{\partial F}{\partial T_2} &= C_2T_2 + 0 + 0 + 0 - \rho = 0 \\
\frac{\partial F}{\partial T_3} &= C_3T_3 + \frac{\lambda}{\sqrt{2}} + \mu + 0 + 0 + 0 = 0 \\
\frac{\partial F}{\partial T_4} &= C_4T_4 + 0 + 0 + \frac{}{\sqrt{2}} + \xi + 0 = 0 \\
\frac{\partial F}{\partial T_5} &= C_5T_5 + 0 + 0 + \frac{\nu}{\sqrt{2}} - \xi + 0 = 0 \\
\frac{\partial F}{\partial T_6} &= C_6T_6 + \frac{\lambda}{\sqrt{2}} - \mu + 0 + 0 + 0 = 0
\end{aligned} \tag{16}$$

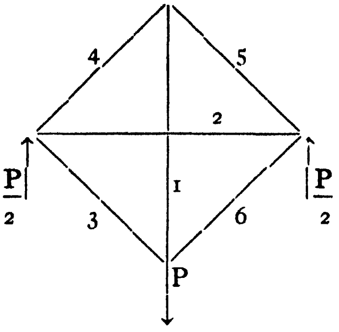

Fig. 1

These equations may be treated as homogeneous equations in the quantities 1, λ, μ, ν, ξ, ρ and the determinant of the coefficients set equal to zero. When the Greek symbols are eliminated and account taken of (14), we have: for T_1; (See Church)[1]

$$T_1 = P \frac{C_2 + C_3 + C_6}{2(C_1 + C_2) + C_3 + C_4 + C_5 + C_6} \tag{17}$$

and likewise for the other five T's.

Here again, as was the case with gas in the equilibrium state, the equations (16) that determine the minimum of U subject to a constant load P are identical with those determining a maximum P subject to a constant U. And hence the Principle of Least Work is the equivalent of a principle of maximum load for given internal energy. Altho exact proportionality between stress and strain holds in a very restricted domain, in general increased tension corresponds to increased strain according to some law or other. Likewise increased load corresponds to increased strain. Hence we see that equations (16) determine the state of maximum strain as well as the state of least work, and we conclude that in the domain of engineering statics as well as gas theory, the Principle of Maximum Strain is equivalent to the Principle of Least Work or Internal Energy.

4. Forces in Velocity and Momentum Space

Altho force is usually thought of as operating only in ordinary space, it is clear that a particle which takes on a change of momentum undergoes a change of position in momentum space and velocity space. Furthermore this change may take place by collisions without alteration of its position in ordinary space. Thus a molecule of gas in equilibrium or an atom of a solid may keep its position of equilibrium in ordinary space while changing its position in velocity space during an interval of time dt. Such a time rate of change of momentum involves, according to Newton's law, the operation of a force. This force which in the absence of displacements does no resultant work in ordinary space, may be thought of as doing work in velocity space or momentum space since the molecule on which it acts takes on a corresponding change of energy as the force acts to change its position in velocity or momentum space. Thus forces must (to the extent that Newton's laws apply to agitated molecules) be thought of as operating not only in ordinary space but in velocity and momentum space.

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[1] I. P. Church· "Mechanics of Internal Work," Chapter III.

The corresponding energy equations take the form:

$$W - W_o = \int_{x_o}^{x} F_x dx. \tag{18}$$

and $$W - W_o = \int_{mu_o}^{mu} mudu. \tag{19}$$

where the limits x and x_o refer to the *same* place in ordinary space at different times and to different places in momentum space where momenta are mu and mu_o respectively. This means that the interval x-x_o over which the integrand is summed, amounts to zero when plus and minus signs are considered, altho physically it is ordinary space thru which the force acts (back and forth.

5. Theorem: The Equations that Determine the State of Maximum Entropy or Probability represent Equilibrium between Stresses and Strains in Velocity or Momentum Space

In this section we show that equations (11) or (16) which determine the state of maximum probability or least internal work, are to be interpreted as equilibrium equations between stress and strain. To do this, we replace λ, the undetermined constant, by its value $-W/kT$ which is determined from the distribution function in the usual way. Then if we transpose and multiply both sides of (11) by $kT\frac{du}{dx}$ and drop the subscripts, we obtain:

$$\frac{kT}{r}\frac{dr}{dx} = mu\frac{du}{dx} = m\frac{du}{dt} = F_x \tag{20}$$

We here view $dx = u\,dt$ as the absolute value of distance travelled (of plus or minus sign) in time dt, whose resultant is taken to be zero, and the du is the change in velocity magnitude, i.e. the change in agitation velocity according to the last section, so that the force referred to acts only in velocity or momentum space. Where molecules are free to move it is always real and finite (zero when the above du is zero); and distinct from the force exerted by the molecules in ordinary space, (this latter will be zero when the plus and minus values of du/dt cancel each other). Equation (20) refers to the individual molecule in the Maxwell distribution where the velocity is u, and if the differential coefficients were known, the magnitude of (20) could be determined.

Since (20) is like (11) an equilibrium equation, and since the right member is the force corresponding to one molecule, the left member must be the reacting force per molecule, which is seen to include the corresponding strain multiplied by the elastic coefficient per molecule.

Thus dr/r is a true strain, i.e., a dimensionless physical quantity, a change in range per unit range. This range is the distance that separates successive molecules in velocity space, (or the excess distance in ordinary space acquired between them in unit time).

The way in which the foregoing fits into the theory of elasticity becomes more clear if we re-call that stress or internal force per unit area may be thought of as internal energy per unit volume. Thus in electrostatics where the field strength is F, the energy per unit volume is given by $F^2/2$ and this is also the expression for tension or ether stress along lines of force. Also for the Pascal case of hydrostatic equilibrium, the pressure p is the potential energy per unit volume, and also represents the three normal stresses. Consider also the isothermal bulk modulus of elasticity p, the ratio between pressure differences and the corresponding change in volume per unit volume:

$$E = \frac{-dp}{dV/V} = p = nkT \qquad (21)$$

Here the dp is a force per unit area that refers not to the Pascal hydrostatic force equal in all directions, but to that stress which is balanced by the strain according to (21), being the *change* in potential energy per unit volume. For the Maxwell distribution of velocities we have from (20):

$$kT = \frac{mu_1du_1}{dr_{1/r_1}} = \frac{mu_2du_2}{dr_{2/r_2}} = \dots\dots = \frac{mu_Ndu_N}{dr_{N/r_N}} \qquad (22)$$

which shows that for gas in equilibrium at temperature T, there is a constant ratio, i.e., an elastic coefficient per molecule, kT which is the ratio between energy difference and corresponding strain for the various positions of a molecule throughout velocity space. As the denominators of (22) are true strains, so it is clear that the numerators are pressure differences due to energy changes, which tend to change the positions in velocity space of molecules on which they act, being balanced by the corresponding strains.

Each position u_i in velocity space is (under equilibrium conditions) maintained by some molecule (or other) under action solely of pressure due to impacts, and this must be an unbalanced force as between molecules of different energy and position in velocity space. Thus the equations (11) which correspond to the Maxwell distribution are seen to be equilibrium equations between the stress and strain in velocity and momentum space. Accordingly this distribution seems to be the result of forces acting in velocity space.

Likewise it will readily be understood that equations (16) can be shown to be the equilibrium equations between stress and strain. (Express the undetermined Greek constants in terms of the y's with the help of (12) and divide by the C's).

6. Magnitude of Stress and Strain acting in Velocity Space, where Thermal Equilibrium prevails, in Gas obeying the Gas Law

The proportion (22) still holds if we sum the numerators and sum the denominators for the n molecules in unit volume:

$$kT = \frac{\Sigma\ mu_i du_i}{\Sigma\ dr_i/r_i} = \frac{nmu\ du}{n\dfrac{dr}{r}} \tag{23}$$

or multiplying by n:

$$nkT = p = \frac{nmu\ du}{dr/r} = \frac{f_u}{dr/r} \tag{24}$$

where the numerator is seen to be the total force for all n molecules per c.c. due to energy differences of molecules that react against each other, and the modulus of elasticity p is the familiar isothermal bulk modulus for gas obeying the gas law according to (21). The numerator f_u is seen to be like the usual $p = \frac{1}{3}(nmv^2) = nmu^2$, except that 2mu of the latter, the change in momentum per impact in the x direction, is replaced by 2mdu, the excess change of momentum that has to be balanced by strain in momentum space.

To calculate the magnitude of the stress f_u above, we note that the differentials in (23) and (24), which generally above have their usual interpretation as variables approaching zero, must be given a special interpretation if the numerators of these equations are to represent the actual stress or total unbalanced pressure due to energy differences. Thus if we take in the manner of elementary kinetic theory, $u_i/2$ as the number of impacts per second and $2mdu_i$ as the unbalanced change in momentum per impact for this component of this molecule, the product gives the excess change in momentum per second or unbalanced pressure as between two molecules at u_i in velocity space. But the r_i used throughout this paper is precisely the expression for velocity (or momentum) differences between successive molecules in velocity space, and it is only when such differences are used in (23) and (24) that the energy differences shown there represent unbalanced pressure of molecules that jostle each other in equilibrium. The same result is reached if no limit is imposed on the arbitrariness of the differentials which might be zero but then the number of molecules would increase indefinitely and still satisfy the distribution law. Thus for the stress or force per unit area in the x direction and acting only in velocity space:

$$f_u = nmu\ du = nmur = nu\frac{(2\pi emkT)^{\frac{1}{2}}}{n} = \sqrt{2\pi e}\ kT \qquad (25)$$

where the momentum range mr for the molecule in its mean energy state is introduced with the help of (4) and $mu^2 = kT$ for one component of the root mean square velocity. Also see the writer's Entropy and Probability[1], equation (38). And likewise the corresponding strain is:

$$\frac{dr}{r} = \frac{2u\ du}{\alpha^2} = \frac{2u(2\pi emkT)^{\frac{1}{2}}}{m\alpha^2 n} = \sqrt{2\pi e}/n \qquad (26)$$

It is noteworthy that no change of T occurs with the differentials of these equations because we are considering changes within gas where temperature equilibrium prevails, and also that the strain is a pure number depending only directly on the density and affected by temperature changes only indirectly according to the gas law.

It is to be emphasized that the stress (25) does not in general operate to change momentum in ordinary space except as applied to motions where the vector sum of the changes in ordinary space is zero, although they add up to increase agitation energy and absolute velocity, thus corresponding to a shift of position in velocity and momentum space. And yet f_u is a true stress in that it acts on unit area like hydrostatic pressure and is an energy difference for the n molecules per unit volume of ordinary space and would cause a time rate of change of momentum (in momentum space) unless balanced as per (24) and (11). Furthermore, it is an isothermal stress like the dp of (21) with the same modulus of elasticity $p = nkT$; and again if we divide both members of (21) by n and interpret dp/n as the pressure difference per molecule, then the elastic modulus per molecule will be kT for (21) as it is in (22).

If there were uniform molecular distribution in velocity space, i.e., if there were equal intervals between successive molecules in velocity space, then dr_i would be zero and there would be no reacting force (kT times the strain) to counterbalance the forces represented by the numerators of (22), (23) and (24). And those forces would operate by elementary mechanics to increase the energy of the slow molecules and reduce the energy of the fast moving ones, thus reducing the intervals r_i by bringing the molecules together in velocity space. But a smaller r_i makes an increased strain (other things being equal) and hence increased reacting force. The condition of equilibrium is thus a stress given by the numerators of (23) and (24) acting in velocity space through forces shown as numerators of (23) that tend to reduce the differences between agitation velocities (to reduce intervals in velocity space), which forces are balanced by the increased strains. Comparison of (21) and (24) shows that molecules "object" to all occupying the same position in velocity space with the same vigor (same modulus of elasticity) that they object to occupying it in ordinary space, and apparently for the same reason, i.e., more of them together in unit interval causes bigger reaction.

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[1] Loc. cit.

7. The Second Law of Thermodynamics

According to this law automatic changes within a closed system always involve an increase of entropy till the equilibrium state of maximum entropy and probability is reached subject to the boundary conditions on the volume and energy of the system. No ergodic hypothesis is needed, according to the present treatment, to account for this fact that the rate of change of entropy is always positive:

$$\frac{dS}{dt} > 0 \tag{27}$$

For we have seen that the state of maximum entropy corresponds to the equilibrium equations between stress and strain in ordinary and momentum space. And likewise the unstable state corresponds to a failure to satisfy the equilibrium equations between stress and strain within the gas. That is to say the stresses within the gas are not completely balanced in the absence of the equilibrium condition of maximum entropy. And this refers to stresses acting in momentum and velocity space as well as ordinary space according to 4 and 5. Thus a gas at uniform temperature and pressure whose molecules were uniformly spaced, but wherein a Maxwellian distribution of velocities did not prevail, would involve stresses acting in velocity space which as pointed out in 6, would not be balanced by the strains corresponding to the equilibrium condition. Hence an immediate rearrangement in velocity space would take place involving a time rate of change of momentum of most of the molecules under the action of internal *forces*, i.e.: stresses would act in velocity and momentum space.

A simple illustration of the second law is found by considering equal quantities (N molecules) of the same type of gas at two *different* temperatures T_1 and T_2 but at the *same* pressure and separated by any conceivable barrier impervious to heat conduction. If we take $T_1 > T_2$ the first gas will occupy more volume than the second (i.e. $V_1 > V_2$) according to the gas law (since there are equal numbers of molecules). Hydrostatic equilibrium prevails since the pressure is taken to be uniform, and we assume that two gases are thermally insulated from the outside world by fixed walls impervious to heat tho separated from each other by a *removable* non conducting barrier. Now remove the imaginary barrier in such a way as not to disturb the two gases by the removal process, and note the operation of the second law of thermodynamics in this container where hydrostatic equilibrium prevails (but not thermodynamic). Molecules of the high temperature gas, having more kinetic energy, will as they impact with those of the cooler gas impart by elementary mechanics some of their kinetic energy to the latter until at length temperature equilibrium prevails at $T = (T_1+T_2)/2$, while the total agitation *energy* of the two gases together remains constant. This increase of energy of the cooler molecules involves time rate of change of momentum and the action of stresses (forces) within the gas to cause that rate of change. And the corresponding increased total strain parallels the known increase of entropy according to (7), (8), and (9). And thruout this change no work is done in ordinary space wherein hydrostatic equilibrium is maintained.

Although no attempt is here made to extend this explanation to the multitudinous complicated cases to which the second law applies, yet it would seem that it would apply and account for the changes of states involved in the workings of the second law in all cases where the relation between entropy and strain is correctly given by (9).

8. Experimental Verification

We note that these relations between entropy, strain and a-priori probability are an immediate consequence of using in Boltzmann's equation the geometrical expression for weight (6) rather than the familiar statistical one. It was pointed out, however, in the writer's Entropy and Probability[1] that these expressions are mathematically equivalent and interchangeable. This makes the problem of distinguishing experimentally between the two points of view a difficult one. For if one starts with two equivalent expressions for entropy, one obtains equivalent theoretical results whenever equivalent mathematical lines of reasoning are applied to the two treatments. The Maxwell distribution of velocities viewed as the most probable distribution may be thought of as brought about spontaneously and explicable in statistics according to the ergodic hypothesis. The present theory indicates however, like *Boltzmann's H-theorem* that it comes about as a result of *forces*. The question arises, are the many so called "spontaneous" *deviations* from equilibrium which involve corresponding changes of entropy also explicable as due to the action of forces? The reasoning of the present paper indicates an affirmative answer for such probability deviations *provided* their probability is of the a-priori Type A and measured according to the probability axioms and related to entropy and strain according to (9) by Boltzmann's relation. There seems to be no case where it has been positively shown that there are no veiled forces to account for "spontaneous" changes in entropy like the veiled forces that the present treatment shows are involved in the Maxwell velocity distribution of maximum probability. The detailed application of this method to fluctuations within gas where a Maxwell distribution of velocities prevails, is planned in a subsequent paper. On the other hand the present theory has nothing to say about fluctuations and changes whose probability is not of Type A and hence not related to Entropy according to (9) by Boltzmann's relation. (See section two above).

The most outstanding verification of the present theory, however, seems to be the second law of thermodynamics itself. The ergodic hypothesis, as an explanation of why gas will go from an unstable, improbable state to the equilibrium state of maximum probability, does not appear satisfactory to most physicists and still presents, according to Tolman[2], "a baffling problem for further study". This marks a sore spot and partial failure in the statistical theory.

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[1] Kimball: loc. cit.

[2] Tolman: "Statistical Mechanics", 21, 39.

On the other hand, forces certainly do act in velocity and momentum space, and, as pointed out herein, may do work in these realms when no work is done in ordinary space, and cause strains there distinct from any strains in ordinary space. Thus, when entropy is viewed as k times the sum of the strains, it is readily suggested that it is the action of these forces that cause the state of maximum entropy and probability to be reached. This mechanical explanation of the second law is calculated to appeal to those who welcome the modern tendency to extend further the application of mechanical principles, as for example to the action of light photons.

The writer is specially indebted to Prof. G. E. Uhlenbeck of the University of Michigan for valuable criticism and discussions.

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TEMPERATURE OF MAXIMUM DENSITY OF AQUEOUS SOLUTIONS. DEVIATIONS FROM THE LAW OF DESPRETZ

BY NORA GREGG-WILSON AND ROBERT WRIGHT

The generally accepted explanation of the phenomenon of the temperature of maximum density of water is derived from the fact that the density of water is greater than that of ice. In common with other liquids the density of water increases with fall of temperature, but as it approaches the freezing point ice molecules are supposed to form and their smaller density to counteract the increasing density of the water. At 4°, the temperature of maximum density (t.m.d.) of water, these two effects just balance, and between 4° and the freezing point the preponderance of ice molecules causes an increasing lowering of the total density.

The t.m.d. of aqueous solutions has been frequently investigated, and the most important generalisation put forward is that due to Despretz,[1] who found that the t.m.d. of water was lowered by the addition of a solute and that the lowering was directly proportional to the concentration of the dissolved substance.

The lowering of the t.m.d. by a solute does not depend, like the lowering of the freezing point, solely on the molecular concentration, but varies also with the nature of the dissolved substance. De Coppet[2] has measured the molecular lowering of the t.m.d., that is the lowering produced by a gram molecule of solute in a litre of solution, for a number of substances and found the result to vary greatly with the nature of the solute employed. In the solutions of simple binary electrolytes it would seem that each ion has its specific effect on the t.m.d., and that the molecular lowering of a salt solution can be calculated from the observed effects of other salts.[3]

All salt solutions which have been investigated, and the great majority of solutions of organic substances, obey the law of Despretz. The important exceptions are the dilute solutions of the lower alcohols;[4] of these ethyl alcohol is the most interesting. With dilute solutions this substance causes a rise of the t.m.d., but with greater concentrations a depression is produced. Solutions of ethyl ether also deviate from the law of Despretz[5] but they do not give an elevation of the t.m.d.

In considering the effect of a solute on the t.m.d. of water three factors should receive attention. The lowering of the temperature of production of ice molecules—i.e. of the freezing point, the temperature coefficient of expansion of the solution, and the density of the solution.

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[1] Ann. Chim. Phys., **70**, 5, 49 (1839); **73**, 296 (1840).

[2] Ann. Chim. Phys., **3**, 246, 268 (1894); Compt. rend., **125**, 533 (1897); **128**, 1559 (1899); **131**, 178; **132**, 1218 (1900); **134**, 1208 (1902).

[3] Wright: J. Chem. Soc., **115**, 119 (1919).

[4] DeCoppet: Compt. rend., **115**, 625 (1892); J. P. McHutcheson: J. Chem. Soc., **129**, 1899 (1926).

[5] Nort: Landolt and Börnstein Tabellen.

Since the lowering of the freezing point depends only on the molecular concentration of the solute, it should be the same for all solutions of organic compounds of equal molecular concentration, though for salt solutions the effect will be greater owing to ionisation of the solute. In all cases the lowering of the freezing point will produce a corresponding lowering in the t.m.d. of the solution.

The coefficient of cubical expansion of any aqueous solution is greater than that of pure water. It therefore follows that the contraction caused by the fall of temperature, which has to be balanced by the formation of ice molecules before the t.m.d. is reached, is greater for a solution than for water, hence the increase in the coefficient of expansion will cause a lowering in the t.m.d.

The effect on the t.m.d. due to the density of the solution depends on whether that density is greater or less than that of water. If the solution has a density greater than that of water, then the separation of ice molecules in the neighbourhood of the t.m.d. will increase the concentration of the remaining solution and the resulting increase of density will have to be balanced by the further production of ice molecules before the t.m.d. is reached. That is, the t.m.d. will be lower on account of the solution being more dense than water. On the other hand if the density of the solution is less than that of water, then the removal of solvent by the formation of ice molecules will still further decrease the density of the remaining solution, and thus help the action of the ice molecules and tend to raise the t.m.d. of the solution.

We thus come to the conclusion that for solutions of greater density than water, all three contributary causes tend to lower the t.m.d.; whilst for other solutions, the lowering of the freezing point and the greater coefficient of expansion, will be to some extent balanced by the smaller density of the solution.

For dilute solutions all three factors, lowering of the freezing point, increase in the coefficient of expansion, and the density of the solution, will be proportional to the concentration of the solute, and therefore their combined effect will also be proportional to the solute concentration and hence the solution will obey the law of Despretz. As a rule with electrolytes all three contributary factors are relatively great, so that only dilute solutions, such as might be expected to obey the law of Despretz, have been investigated. With more concentrated solutions the t.m.d. is in general lower than the freezing point.

Solutions of hydrochloric acid and lithium chloride are however exceptions to the general class of electrolytes, since the molecular lowering of the t.m.d. (as calculated from dilute solutions) is in the neighbourhood of six degrees. These solutions were therefore examined up to a concentration of 2N with the result shown in the table:

N	Hydrochloric acid lowering of t. m. d.	N	Lithium chloride lowering of t. m. d.
0.5	2.9	0.5	2.7
1.0	6.9	1.0	5.9
2.0	16.4	2.0	12.5

It is at once obvious that at high concentrations the law of Despretz is not obeyed. This result is probably related to the well-known phenomenon of the excessive lowering of the freezing point which occurs with concentrated electrolyte solutions.[1]

With solutions of organic compounds the coefficient of expansion is generally less than that of salt solutions of a corresponding molecular concentration, and the depression of the freezing point owing to the absence of ionisation) will also be less. Further, if we confine our attention to those substances which give solutions of less density than that of water, we are dealing with a class of solution of which the molecular lowering of the t.m.d. will be the smallest possible. As a consequence we should be able to employ fairly concentrated solutions and have a good opportunity of observing deviations from the law of Despretz.

The number of organic compounds less dense than water, and at the same time sufficiently soluble, is considerably restricted. Apart from the alcohols, which have already been investigated, the most important group is that of the fatty amines. The values of the t.m.d. for a number of amines have been determined and the results are tabulated along with those obtained for a few other substances. It will be seen that in general there is a deviation from the law of Despretz for the stronger solutions, and that the deviation is in the direction of excessive lowering of the t.m.d.

The relative densities at 5° have also been tabulated and so have the coefficients of expansion between the temperatures 12.5° and 15°. The densities when plotted against the concentrations give approximately linear graphs, but the coefficients of expansion as a rule show excessive increases with increase of concentration. This abnormal increase in the coefficient of expansion is made clear by the table of "Molecular increase of coefficient of expansion", in which is given the values for $\frac{a_s - a_w}{N}$ where a_s is the coefficient of expansion of the solution, a_w that of pure water and N the concentration of the solute in gram molecules per litre. If the change in the coefficient of expansion was directly proportional to the concentration, then the value of $\frac{a_s - a_w}{N}$ should be constant. It will be seen however that for most solutions it tends to increase, and it is to this excessive increase in the coefficient of expansion with the more concentrated solutions that the excessive lowering of the t.m.d. is to be attributed.

Three substances among those investigated call for special mention. Ethyl alcohol, as already pointed out, first raises the t.m.d. and then lowers it. The coefficients of expansion of the alcoholic solutions are very near those for pure water in the case of solutions up to N/2 strength. So that for this substance the factor due to the small density of the solution outweighs the others in the case of dilute solutions, but at higher concentrations the increasing coefficient of expansion causes a lowering of the t.m.d. For aceto-nitrile, up

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[1] Biltz: Z. physik. Chem., 40, 185 (1902); Jones: Carnegie Soc. Reprint 60 (1907.)

Lowering of Temperature of Maximum Density

	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$	$(C_2H_5)_2NH$	CH_3CN	$(CH_3)_2CO$	C_2H_5OH	
N/8	0.2°	0.1°	0	0.1°	0.2°	0.1°	0.9°	0.4	−0.15	N/8
N/4	0.4°	0.2°	0	0.3°	0.4°	0.4°	1.6°	1.0	−0.20	N/4
N/2	1.1°	0.6°	0.5°	1.2°	1.2°	1.4°	3.5°	2.3	−0.20	N/2
N	2.4°	1.8°	2.6°	5.2°	3.2°	4.9°	7.3°	6.2	0.3	N
2N	5.4°	6.4°	10.2°	—	11.1°	14°	14°	—	3.8	2N

Relative Density at 5°C.

	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$(C_2H_5)_2NH$	CH_3CN	$(CH_3)_2CO$	$C_2H_5NH_2$	C_2H_5OH	
N/8	.9988	.9990	.9987	.9970	.9988	.9982	.9991	.9995	.9986	N/8
N/4	.9979	.9977	.9970	.9951	.9974	.9963	.9988	.9988	.9977	N/4
N/2	.9959	.9957	.9934	.9910	.9945	.9926	.9972	.9968	.9956	N/2
N	.9922	.9912	.9870	.9822	.9895	.9872	.9954	.9936	.9915	N
2N	.9851	.9826	.9765	——	.9805	.9759	.9908	——	.9856	2N

Coefficient of Expansion 12.5° and 15°C

	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$	$(C_2H_5)_2NH$	CH_3CN	$(CH_3)_2CO$	C_2H_5OH	
N/8	.0001375	.0001360	.0001350	.0001375	.0001350	.0001350	.0001470	.0001363	.0001365	N/8
N/4	1415	1378	1360	1410	1350	1358	1550	1440	1380	N/4
N/2	1480	1432	1422	1574	1447	1565	1800	1670	1405	N/2
N	1610	1592	1690	2095	1725	2043	2220	1953	1495	N
2N	2310	2024	2450	——	2480	4037	3260	——	1900	2N

Molecular Increase of Coefficient of Expansion $\frac{\alpha_s - \alpha_w}{N}$

	NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$	$(C_2H_5)_2NH$	CH_3CN	$(CH_3)_2CO$	C_2H_5OH	
N/8	.0000200	.0000080	.0000000	.0000200	.0000000	.0000000	.0000960	.0000104	.0000120	N/8
N/4	260	112	40	240	000	32	800	360	120	N/4
N/2	260	164	150	448	294	430	900	640	110	N/2
N	260	242	340	645	375	693	870	600	145	N
2N	480	337	550	——	565	1343	905	——	275	2N

to 2N concentration, the coefficient of expansion is directly proportional to the concentration, and hence this substance obeys the law of Despretz. The same is true for ammonia but only up to N concentration.

The above results indicate clearly that the law of Despretz, like so many other generalisations, only holds in the case of dilute solutions and breaks down as soon as the solutions become concentrated.

Experimental. The determinations of the t.m.d. were carried out by means of a compensated dilatometer in the manner already described by one of us.[1] The coefficients of expansion were made with the same instrument, the stem being calibrated for the purpose. The choice of the temperature range 12.5° to 15° is an arbitrary one, but it was considered to be sufficiently removed from the t.m.d. to be free from the complication of the formation of ice molecules. The coefficient was calculated from the expression $a = \frac{V_{15} - V_{12.5}}{2.5 \times V_{12.5}}$ where V_{15} and $V_{12.5}$ are the volumes at 15 and 12.5 respectively.

In conclusion it should be recalled that the t.m.d. is not capable of exact determination and hence the above data are only approximate. Nevertheless there can be no doubt that the conclusion that the law of Despretz only holds for dilute solutions is correct.

Physical Chemistry Laboratory,
University of Glasgow.
July 1, 1930.

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[1] Wright: J. Chem. Soc., **115**, 119 (1919).

INFLUENCE OF ELECTROLYTES ON THE SYNERESIS AND CLOTTING OF BLOOD

BY SATYA PRAKASH AND N. R. DHAR

In a previous communication,[1] we have advanced the view that clotting of blood and jelly formation are essentially similar processes. Blood may be regarded as an unstable colloidal system which remains fluid in the body partly due to its motion and partly to the capillary action of the blood vessels.

We[2] have investigated the influence of various electrolytes on the time of setting of jellies as well as on the extent of syneresis with numerous inorganic and some organic jellies. Moreover we have shown that a sol is stabilised by the adsorption of similarly charged ions and is sensitised by the oppositely charged ions, and under similar conditions, the uncharged particles are more hydrated than the charged ones. By the adsorption of similarly charged ions, the charge on the particles increases and the system becomes more stable, less viscous, and less hydrated.

Blood is regarded as a negatively charged fibrin sol, which exists in the liquid condition in some mysterious way. When it is collected in a glass vessel, it spontaneously forms a solid clot within a few minutes, but it is well-known that if it is received in solutions of sodium, or ammonium oxalate, fluoride or citrate, it can remain liquid indefinitely, and further if calcium chloride is added in excess to the oxalated or citrated blood, the clotting occurs normally. As normal blood also contains calcium, this behaviour was ascribed to the formation of insoluble or undissociated calcium salts of citrated and oxalated blood and thus to the removal of calcium ions. We have shown in the previous communication that blood has a great tendency to adsorb similarly charged ions from such electrolytes as sodium acetate, tartrate and citrates, and also potassium fluoride and oxalate, and the stabilising influence of the salt is due to this fact and not to the removal of calcium ions.

In the present communication, we have investigated the influence of the concentration of electrolytes on the extent of syneresis and have shown that blood is markedly stabilised by the addition of calcium chloride.

For these experiments on the syneresis of blood-clot, goat's blood was received in 250 c.c. glass bottles containing different amounts of electrolytes and made up to a definite volume. A blank experiment was always performed with the same blood, as the blood from different animals behaves slightly differently. After definite intervals, synerised serum was carefully collected in a graduated measuring cylinder and the volume was measured. The experiments were carried at the room temperature (27°-29°). The results are recorded in the following tables:

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[1] J. Phys. Chem., 33, 459 (1929).

[2] J. Indian. Chem. Soc., 6, 587 (1929); 7 (1930).

TABLE I

Influence of Dilution of Syneresis

Time	Amount of syneresis 250 c.c. blood	 230 c.c. blood + 20 c.c. water
30 minutes	9 c.c.	28 c.c.
1 hour	30	58
1 hour 30 minutes	47	77
2 hours 30 minutes	67	99
3 hours 30 minutes	83	112
4 hours 30 minutes	93	118
5 hours 30 minutes	98	122
17 hours	127	151
22 hours	129	141

The serum when no water was mixed was straw-coloured, but in the presence of water, blood was hemolysed and the serum was dark red.

TABLE II

Influence of Potassium Chloride on Syneresis

5 c.c., 10 c.c. and 15 c.c. of 3N potassium chloride made up to 20 c.c. were taken into bottles in which 230 c.c. blood were received. In the blank bottle, 20 c.c. of water and 230 c.c. of blood were taken.

Time		Amount of syneresis		
KCl	0	5 c.c.	10 c.c.	15 c.c.
30 min.	10 c.c.	16 c.c.	2 c.c.	0.5 c.c.
1 hr.	38	30	5	1.0
1 hr. 30 min.	50	48	5	3
2 hr. 30 min.	67	63	7	4
3 hr. 30 min.	83	74	7.5	4.5
4 hr. 30 min.	93	81	8	5
5 hr. 30 min.	98	83	8	7
21 hr.	128	127	8	8

Hemolysis was checked in the presence of potassium chloride and the serum was straw coloured.

TABLE III

Influence of Calcium Chloride on Syneresis

Concentration of calcium chloride = 1.76 M

Blood = 230 c.c. Total volume = 250 c.c.

Time	Amount of syneresis				
$CaCl_2$	0	5 c.c.	6 c.c.	7 c.c.	8 c.c.
30 min.	2 c.c.	0.2 c.c.	0	not set	not set
1 hr.	21	0.2	0	just set	not set
1 hr. 30 min.	51	0.2	0.1	0	not set
2 hr. 30 min.	73	0.2	0.1	0	not set
3 hr. 30 min.	86	0.2	0.1	0	not set
4 hr. 30 min.	92	0.7	0.1	0	not set
5 hr. 30 min.	92	1.0	0.1	0	not set
13 hr. 30 min.	108	2.0	1.0	0.5	—
21 hr. 30 min.	110	7.0	—	—	just set
48 hrs.	—	—	—	—	3 c.c.

TABLE IV

Influence of Ammonium Sulphate on Syneresis

Concentration of ammonium sulphate = 2M

Blood = 230 c.c. Total volume = 250 c.c.

Time	Amount of syneresis			
Am_2SO_4	0	5 c.c.	8 c.c.	11 c.c.
30 min.	28 c.c.	29 c.c.	2 c.c.	not set
1 hr.	59	56	15	just set
1 hr. 30 min.	70	71	17	2
2 hr.	81	82	64	8
3 hr. 30 min.	102	103	84	27
4 hr. 30 min.	102	108	92	36
5 hr. 30 min.	108	113	94	41
13 hrs.	119	128	117	52
17 hrs.	122	128	118	55

TABLE V

Influence of Potassium Oxalate on Syneresis

Concentration of potassium oxalate = N

Blood = 230 c.c. Total volume = 250 c.c.

Time	Amount of syneresis			
Potassium oxalate	0	2 c.c.	3 c.c.	4 c.c.
30 min.	10 c.c.	10 c.c.	not set	not set
1 hr.	57	57	2 c.c.	half set
1 hr. 30 min.	85	68	4	half set
2 hr.	96	70	5	just set
3 hr. 30 min.	115	75	8	2 c.c.
4 hr. 30 min.	118	78	12	4
5 hr. 30 min.	121	78.5	13	5

TABLE VI

Influence of Sodium Acetate on Syneresis

Concentration of sodium acetate = N

Blood = 230 c.c. Total volume = 250 c.c.

Time		Amount of syneresis		
Sodium acetate	0	2 c.c.	4 c.c.	6 c.c.
30 min.	20 c.c.	30 c.c.	32 c.c.	39 c.c.
1 hr.	31	56	66	62
1 hr. 30 min.	66	75	84	78
3 hr. 30 min.	100	105	115	112
4 hr. 30 min.	108	108	118	117
5 hr. 30 min.	115	111	122	121
20 hrs.	130	111	135	135

TABLE VII

Influence of Sodium Tartrate on Syneresis

Concentration of sodium tartrate = N

Blood = 230 c.c. Total volume = 250 c.c.

Time		Amount of syneresis		
Sodium tartrate	0	2 c.c.	4 c.c.	6 c.c.
30 min.	6 c.c.	34 c.c.	42 c.c.	32 c.c.
1 hr.	64	62	67	52
1 hr. 30 min.	77	77	80	66
2 hr.	82	84	86	74
2 hr. 30 min.	92	93	94	80
3 hr. 30 min.	106	102	107	91
4 hr. 30 min.	111	105	113	93
16 hrs.	120	120	125	113

TABLE VIII

Influence of Sodium Citrate on Syneresis

Concentration of sodium citrate = N

Blood = 230 c.c. Total volume = 250 c.c.

Time		Amount of syneresis		
Sodium citrate	0	2 c.c	4 c.c.	6 c.c.
30 min.	26 c.c.	31 c.c.	half set	not set
1 hr.	61	62	half set	not set
1 hr. 30 min.	86	70	half set	not set
2 hr. 30 min.	109	94	half set	not set
3 hr. 30 min.	120	113	just set	not set
4 hr. 30 min.	121	116	0	not set
14 hrs.	—	—	10 c.c.	loose clot disturbed

TABLE IX

Influence of Potassium Fluoride on Syneresis

Concentration of potassium fluoride = 4.08 N

Blood = 230 c.c. Total volume = 250 c.c.

Time	Amount syneresis			
K_2F_2	0	1 c.c.	3 c.c.	5 c.c.
30 min.	21 c.c.	7 c.c.	not set	not set
1 hr.	56	14	setting begins	not set
1 hr. 30 min.	80	22	loose clot	not set
2 hr. 30 min.	97	30	0	not set
3 hr. 30 min.	104	39	0	not set
4 hr. 30 min.	111	44	0	setting begins
14 hrs.	122	50	7	0

TABLE X

Influence of Sodium Hydroxide on Syneresis

Concentration of sodium hydroxide = 2.47 N

Blood = 230 c.c. Total volume = 250 c.c.

Time	Amount of syneresis			
NaOH	0	2 c.c.	5 c.c.	8 c.c.
30 min.	19 c.c.	6 c.c.	not set	not set
1 hr.	53	17	not set	not set
1 hr. 30 min.	61	25	not set	not set
2 hr.	84	30	not set	not set
3 hr.	98	42	not set	not set
4 hr.	104	47	not set	not set
4 hr. 30 min.	—	—	setting begins	not set
5 hr.	110	54	sets	not set
17 hr.	122	65	firm clot, no syn. in 2 days	not set

Our results on the syneresis of blood recorded in the above tables show that as the concentration of electrolytes is increased, the amount of syneresis gradually decreases and in some cases the syneresis of blood clot is totally stopped. Even in two days, no marked syneresis is observed. In some cases, with the increase in the concentration of electrolytes, the blood becomes so stable that it either sets after a long time or it does not set at all.

In a previous communication,[1] we have investigated the influence of the concentration of electrolytes on the syneresis of various inorganic jellies. We have shown that as the concentration of the coagulating electrolytes, i.e., those electrolytes from which ions containing charge opposite to that of the sol are mostly adsorbed, is increased, the amount of syneresis is increased.

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[1] J. Indian. Chem. Soc. (1930).

From our results we have also shown, that by increasing the concentration of coagulating electrolytes the time of setting of jellies is much decreased.

The behaviour of blood is quite contrary to that of the jelly-forming inorganic sols. It possesses a high tendency to adsorb similarly charged ions, i.e., anions; and does not appear to adsorb cations to a marked extent. For this reason, the addition of electrolytes invariably stabilises blood. The function of stabilising ions in the cases of jellies is to increase the original time of setting and decrease the extent of syneresis. Thus on increasing the concentration of the stabilising electrolytes, the following may happen:—

(i) Up to a certain limit—no marked influence on the extent of syneresis of the original clot.

(ii) Up to the second limit—gradual decrease in the amount of syneresis.

(iii) Within the next limited range—total inhibition of syneresis.

(iv) Above this limit—blood not clotting at all, but remaining fluid indefinitely.

Hence the function of stabilising electrolytes is just opposite to that of the coagulating electrolytes. From our observations, it will be seen that blood has a high tendency to adsorb chloride, sulphate, oxalate, citrate, fluoride and hydroxyl ions, and in presence of these, the amount of syneresis is markedly decreased. Acetate and tartrate ions do not possess much stabilising influence. In the following table, the comparative influence of acetate, tartrate, citrate and oxalate has been recorded.

TABLE XI

Concentration of salts = N

Blood = 230 c.c. Total volume = 250 c.c.

4 c.c. of N salts have been mixed with blood

Time	Amount of syneresis			
	Sodium acetate	Sodium tartrate	Sodium citrate	Potassium oxalate
30 min.	32 c.c.	42 c.c.	half set	not set
1 hr.	66	67	half set	half set
1 hr. 30 min.	84	80	half set	half set
3 hr. 30 min.	115	107	just set	2 c.c.
4 hr. 30 min.	118	113	set, no syn.	4 c.c.
5 hr. 30 min.	122	—	0	5

From this, it will be seen that the stabilising influence of these ions is in the following decreasing order:

citrate > oxalate > tartrate > acetate.

Our results on the influence of calcium chloride on the syneresis of blood clot show that even in presence of calcium, chloride ions are preferentially adsorbed, and the view that the stabilising influence of citrate, oxalate, fluoride, and other anions is due to the removal of calcium ions appears to be incorrect. We have shown that by increasing the concentration of calcium chloride also, blood is much stabilised, and the amount of syneresis is markedly decreased, and at higher concentrations, blood does not set at all. This is due to the high tendency for the adsorption of chloride ions, as has been observed in the case of potassium chloride also.

In Table XII we are indicating the approximate concentrations of various salts necessary to stabilise the blood to such an extent that no marked syneresis may occur after formation of the clot within 12 hours.

TABLE XII

Electrolyte	Concentration to give clot undergoing no marked syneresis
Potassium chloride	0.12 N
Calcium chloride	0.0845 N
Ammonium sulphate	0.176 N
Potassium oxalate	0.016 N
Sodium citrate	0.016 N
Potassium fluoride	0.049 N
Sodium hydroxide	0.039 N

From the table it will be seen that the stabilising influence of these salts is in the following decreasing order:

$$Na_3Cit > K_2Oxalate > NaOH > K_2F_2 > CaCl_2 > KCl > Am_2SO_4$$

From this order it appears that the stabilising influence depends both on the valency of the ions and alkalinity of the medium.

The clotting of blood has generally been regarded as the conversion of soluble fibrinogen to insoluble fibrin under the action of an enzyme known as thrombin. We are of the opinion that thrombin may assist the process of clotting but it is not essentially the cause of the phenomenon. The clotting of blood is guided by the same forces which bring out the gelation of other organic and inorganic jellies. Fibrin has a high hydration tendency and yields an unstable colloidal suspension. The clotting of blood is guided by the characteristic unstable nature of fibrin, its concentration, and the nature and concentration of electrolytes present in blood, and all this has been so well regulated in blood, that as soon as the capillary action of blood-vessels and circulatory motion are stopped, jelly-forming forces begin to act and finally a solid clot is obtained in a few minutes. The presence of an excessive amount of coagulating electrolyte causes the agglomeration of particles, and the contraction of the clot and the synerised serum is squeezed out of the network. Such syneresis has been observed with various inorganic jellies, such as those of vanadium pentoxide, silicic acid, ferric arsenate, borate and various zirconium jellies. These jellies on ageing, lose markedly the hydration capacity, and on account of the agglomeration of particles give out the solvent.

In previous communications[1] from these laboratories, we have mentioned that the process of jelly formation is guided by the agglomeration and hydration tendencies of the particles. In presence of coagulating electrolytes, the charge on the jelly-forming sol decreases and the amount of hydration increases up to a limiting value. When the concentration of the electrolyte is increased, agglomeration of the particles begins, with the result that the jelly contracts and undergoes syneresis. The same is applicable to the blood clot also. Under the action of coagulating ions, blood forms a clot, and due to the presence of an excess of the same ions, its particles agglomerate and undergo contraction, and finally the serum is squeezed out.

Waele[2] has shown that the blood-fibrinogen exists in a highly buffered system, of which the pH, however, is subject to variations. He has also observed that fibrinogen is precipitated at pH 5-6, forms a gel at pH 7-9, and remains dissolved at pH 10. This dissolution of fibrinogen can be explained on the view that it is stabilised by the adsorbtion of similarly charged OH' ions from the alkaline medium. The observations of Herzfeld and Klinger[3] that acids accelerate the precipitation of fibrin and alkalis exert an inhibitory action can also be explained on the same basis. As we have mentioned in a previous paper,[4] the clotting tendency of blood is most marked near the neutral point. On the acid side and alkaline side, the charge on the blood is increased and hence the hydration tendency is less. Stuber and Heim[5] have observed that the coagulating action of fatty acids increases with the increasing number of carbon atoms in the acids, i.e., in the decreasing order of the dissociation constants. The fall in the coagulating action of the lower members of the series is due to the fact that comparatively larger amounts of hydrogen ions are given out in the presence of these acids and the medium becomes acidic, whereby the charge on the plasma is increased and the system is stabilised.

Summary

1. The influence of different concentrations of potassium chloride, calcium chloride, ammonium sulphate, potassium fluoride, potassium oxalate, sodium acetate, tartrate, citrate, and hydroxide on the extent of syneresis of blood clot has been studied.

2. It has been observed that in all the cases, the amount of syneresis decreases as the concentration of the electrolytes is increased. In some cases, the syneresis is totally stopped and in a few cases, the electrolytes prevent the clotting of blood.

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[1] J. Indian. Chem. Soc., 6, 391 (1929).

[2] Ann. physiol. physico chim. biol., 3, 94 (1927).

[3] Biochem. Z., 71, 391 (1915).

[4] Loc. cit.

[5] Biochem. Z., 77, 333 (1916).

3. The influence of electrolytes is explained on the view that blood has a high tendency of adsorbing similarly charged ions from the salts, and thus the electric charge on blood is increased and it is stabilised. The stabilising influence of the salts is in the following order:

Sodium citrate > potassium oxalate > NaOH > K_2F_2 > $CaCl_2$ KCl > Am_2SO_4.

4. It has been shown that the stabilising influence of fluorides, citrates or oxalates is not due to the removal of calcium ions from the blood, but it is due to the stabilising influence of anions which are largely adsorbed by blood.

5. The syneresis and clotting of blood are guided by the same forces which give rise to the syneresis and formation of inorganic and organic jellies.

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June, 1930.

STUDIES ON THE POROUS DISC METHOD OF MEASURING OSMOTIC PRESSURE[1]

BY F. T. MARTIN AND L. H. SCHULTZ

Introduction

The osmotic pressure of a solution because of its magnitude, should be the most sensitive method available for determining the escaping tendency of the solvent.

The use of a semipermeable membrane, in making this measurement, is difficult because there is no certainty that it will act as a simple sieve. Furthermore it is practically impossible to obtain a membrane impermeable to all ions.

The method of Frazer and Patrick[2] in which tension is exerted on the solvent by means of a porous disc is not beset by these difficulties. It is more straightforward from a theoretical standpoint and so long as the solute is nonvolatile the true escaping tendency of the solvent is certainly being measured. The Donnan membrane equilibrium is also eliminated making the accurate measurement of the osmotic pressure of colloidal solutions a possibility.

On the other hand, while the membrane is eliminated in the porous disc method, other difficulties arise. Air-free or nearly air-free conditions must prevail. The temperature must remain quite constant and a great many other small sources of error must be eliminated.

It was the object of this investigation to study the porous disc method of measurement and to remove, as far as possible, the various difficulties encountered. To this end the original method of Townend was considerably modified and several pieces of special apparatus were developed.

The Thermostat

A drawing of the thermostat, used in this work, is shown in Figure 1. The main bath was a copper tank a meter high and a meter in diameter. It was insulated with "ozite" and was provided with a window about 9 centimeters wide and 41 centimeters long. The propeller, run by the motor M, stirred the water upward.

The thermoregulator T consisted of a long helix of ¼″ copper tubing filled with toluene prepared by the method of Beal and Souther.[3] It was provided with an oscillating contact as described by Gouy,[4] and sparking was avoided at the contact by using a radio tube as a relay.[5]

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[1] This paper is abstracted from two dissertations submitted by the authors to the Board of University Studies of the Johns Hopkins University as part of the requirement for the degree of Doctor of Philosophy.

[2] R. V. Townend: J. Am. Chem. Soc., **50**, 2958 (1928).

[3] J. Am. Chem. Soc., **49**, 1994 (1927).

[4] J. Phys., **6**, 479 (1897). Also Sligh: J. Am. Chem. Soc., **42**, 60 (1920).

[5] Beaver and Beaver: Ind. Eng. Chem., **15**, 359 (1923).

The bath was continuously cooled with water at a constant temperature flowing at a constant rate from a small secondary thermostat thru the coil C. The heat input thru the heater H was governed by the regulator T.

When necessary the water in the small thermostat was cooled with water from a silica gel refrigerator.

The main thermostat was kept at about 27°, the secondary thermostat at about 21° and the water in the refrigerator tank at about 5°. When the

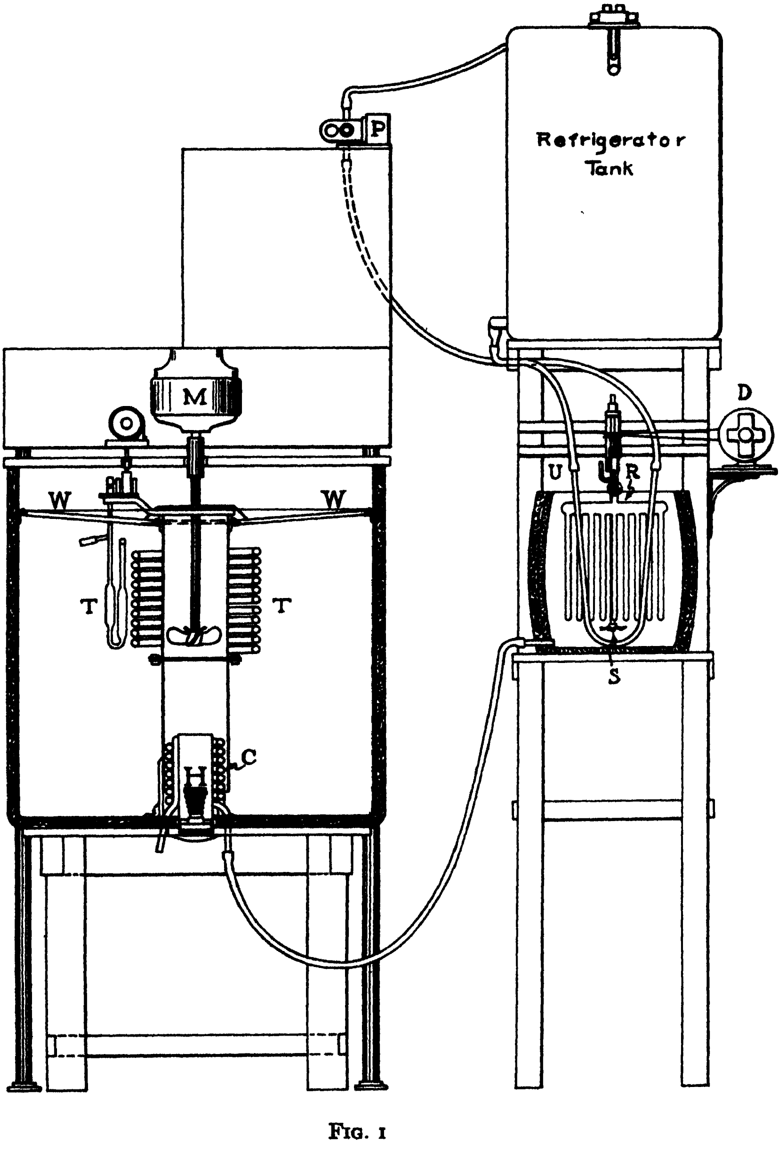

Fig. 1

bath was operating properly a Beckmann thermometer that could be read to 0.001° indicated no change in temperature altho it was tapped vigorously with a special "tapper".

Glass Apparatus and Method of Procedure

The glass apparatus is shown in Fig. 2. The tube 1 led to a mercury vapor diffusion pump backed by a Nelson oil pump. The pumps were protected by the trap 2 which could be surrounded by a mixture of solid carbon dioxide and ether.

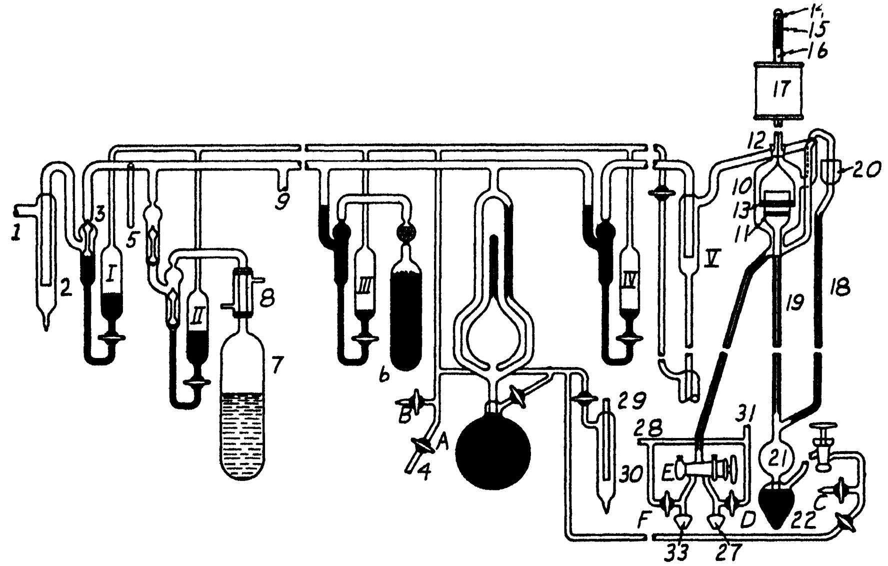

FIG. 2

The mercury cut-offs I, III, and IV were each provided with a stopper 3 which fit into a ground seat when the mercury was raised. Atmospheric pressure could be exerted on the mercury in the left hand limb of these cut-offs while a vacuum was maintained to the right. These cut-offs together with the McLeod gauge etc. were operated by means of a "secondary system" which could be evacuated with a Hyvac oil pump thru the tube 4 and the stopcock A. Air entered the secondary system thru stopcocks B and C.

It was necessary to remove practically all permanent gases from the system before satisfactory measurements could be made. Only under these conditions would the water stick to the disc. Permanent gases also interfered with the process of distillation whereby contact was made between the pure solvent and the solution. This was especially true when vapor was passing from the solution thru the disc into the solvent.

Owing to the fineness of the pores of the disc the removal of air from it was extremely slow, especially as no means were provided for baking the disc while it was being evacuated.

The vacuum pumps reduced the pressure of the gases in the system to less than 1×10^{-5} mm. A more complete removal of permanent gases was accomplished by exposing the system to the cocoanut charcoal contained in bulb 6. The charcoal was prepared by evacuating and heating it to 480° for four or five hours. When opened to the disc it was immersed in liquid air. After 28 days of such treatment (during which time the accumulation of air on standing progressively diminished) a pressure of 10^{-4} mm. developed in two days. The disc as finally used was deaerated 42 days.

Air-free Water. It was, of course, necessary to use air-free water under the disc. Ordinary distilled water was boiled to ¼ its volume to remove most of the air. It was then introduced into the bulb 7 (and another similar bulb at 9) thru a side arm (not shown) which was then connected to a vacuum and sealed off while the water was boiling thru it. The bulbs were kept warm and the water was continuously refluxed by using the small condenser 8. The vapor and accumulated air were removed from time to time by expanding them into the outer system. Four hours after introduction the pressure of the accumulated air was 2.5×10^{-5} mm. After 86 days of deaeration, the air which accumulated in five days gave a pressure in the system of 2×10^{-5} mm. This water was entirely satisfactory for use under the disc.

Freezing and sublimation methods of deaeration were also tried, but we found none of them as good as the above procedure.

The Osmometer. The cut-off IV was just outside the thermostat and was used to protect the osmometer. Another cut-off V inside the bath and under water kept water vapor from getting out of the apparatus in the thermostat.

The main part of the apparatus was the osmometer. It consisted of a flask 10 made of pyrex tubing 7.5 cm. in diameter. Inside this was a sort of funnel holding the porous disc 11.

The flask 10 was fitted with a ground glass stopper 12 that could be mercury sealed. The joint was not greased. The stopper had a long tube sealed to it which stuck up out of the thermostat. It contained the mechanism for operating the platinum gauze stirrer 13 by means of the solenoid 17 and a suitable commutator.

The manometer for measuring the osmotic pressure consisted of the capillary tubes 18 and 19.

The Porous Disc. The porous disc was made of a special clay and ground[1] pyrex glass. Both clay and pyrex were passed thru a 200 mesh sieve. Equal parts by weight were then carefully mixed and water was added to make a not too stiff paste. From this the discs were molded in a plaster of Paris mold. They were about 3 cm. in diameter and 2 mm. thick. It may be mentioned that a mixture containing 75% pyrex was unsatisfactory.

A layer of fine sand was now placed on the bottom of a large porcelain crucible. After making the surface of this sand quite flat the disc was carefully placed on it and covered with more sand which was made flat on top. Another disc could now be laid on this surface and covered with sand.

In this way as many as four discs could be placed in a horizontal position in the crucible. Besides making it possible to bake four discs at once, this arrangement made the heating of the discs more even, their cooling slower, and minimized warping.

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[1] Townend: J. Am. Chem. Soc., 50, 2961 (1928).

The crucible was now heated in a small electric pot furnace, and the temperature being slowly raised to 950°, which is somewhat above the melting point of pyrex. It was held at this temperature for 45 minutes when the current was turned off and the discs were allowed to cool in the furnace.

The baked discs were very hard and quite porous and it was usually unnecessary to grind their faces to get rid of imperfections. However, it was very important to grind the edges of the discs smooth on a large grindstone. If this was not done the discs could not be sealed into pyrex funnels, but if they were ground properly, this operation was very easy and successful.

The discs after being sealed into their funnels were tested by filling the space under the disc with water. A capillary tube also filled with water was then attached and its other end was dipped into mercury. Air was now blown over the disc and if the mercury rose in the capillary to more than the height required for the apparatus, the disc was satisfactory.

Cleaning the Osmometer. The measurements of osmotic pressure were carried out on dilute aqueous solutions of potassium chloride. The concentration of the solutions could not exceed 0.007 molar because of the dimensions of the apparatus. As it was desired to carry the determinations of osmotic pressure to solutions of extreme dilution, great care was taken to thoroughly cleanse the disc, the osmometer and the mercury used in it. The osmometer assembly was washed successively with a mixture of nitric and chromic acids, dilute nitric acid, and conductivity water until a sample of the washings draining thru the disc in two days showed a specific conductance of 1.3×10^{-6} mohs. A check sample of the same water a little better protected from the air had a conductance of 1×10^{-6} mhos.

The mercury used was first treated in turn with dilute nitric acid and distilled water in a dropping column. It was then redistilled and washed repeatedly with conductivity water.

Preparation for making a Measurement. To prepare for making a measurement, air-free water was first distilled from the bulb 7 to the top of the capillary 18 by allowing cold water to flow into the cup 20. Thence the air-free water ran down 18 to the bulb 21. When a little more than was sufficient to fill the space under the disc had collected, the water was forced up thru the disc, by regulating the air pressure over the mercury in the bulb 22, until the mercury in the tube 19 was one or two centimeters below the top of the capillary portion. The excess water on top of the disc and in the tube 18 was then distilled into the condenser tube 5 by surrounding it with ice.

When necessary additional water could be added to that under the disc by carefully introducing small portions into the bulb 21 and then forcing them up thru the capillary 19 at the top of which the water would pass around the mercury.

Once the water was stuck to the disc the level of the mercury in the outer capillary could be changed at will resulting in the application of various tensions to the column under the disc. The level of the mercury meniscus in the capillary 19 varied slightly when the tension was changed due to readjustment of the water surfaces in the capillaries of the disc to the position of equilibrium.

Preparation of the Solution. The potassium chloride used for preparing the solutions was "Kahlbaum for analysis" and was twice recrystallized from conductivity water with pure hydrogen chloride.

The conductivity water was made by distilling ordinary distilled water containing neutral permanganate. The still was of the type described by Dexter[1] and consisted of a large pyrex flask with a block-tin cap connected to a pyrex settling column by a block-tin tube. The condenser was also of block-tin. The flask was heated electrically. The water obtained from this still in one operation and without taking any special precautions usually had a conductivity of 10^{-6} mohs.

Since the solution cup held about 60 cc. and the highest concentration to be used was 0.007 molar, approximately 32 mg. of salt were dissolved in 150 cc. of conductivity water. The solution was slowly boiled down to about 65 cc. in a pyrex flask on an electric heater in order to remove air from it.

Introduction of the Solution into the Osmometer. The hot solution was put into the "solution introducer" Fig. 3. This consisted of a bulb 23 for holding the solution and a mercury reservoir 24 which was set in a wooden block 25. The whole was supported from a large tripod by three springs in the manner indicated by the arrows. The neck of the bulb 23 had a seat 26 ground to fit the stopper 27 (Fig. 2). By means of thumb nuts fastened to the springs the "solution introducer" could be brought up to the stopper 27 and after a little manipulation the ungreased joint could be sealed with mercury.

The vapors above the warm solution were removed by evacuating several times thru the stopcock D and the tube 28 (Fig. 2) which was connected to the tube 29 thru pressure tubing. The Hyvac pump was protected by the trap 30 which was surrounded by solid carbon dioxide. Tube 32 (Fig. 3) was connected thru a two-way stopcock and suction tubing to tube 31 (Fig. 2) so that the space over the mercury in bulb 24 (Fig. 3) was evacuated at the same time as the space above the solution.

When no air bubble was observed, on forcing the solution up against the stopcock E (Fig. 2) the liquid was allowed to cool and was then forced up thru the stopcock E into the osmometer until its surface in the flask 10 was a little above the level of the disc. The solution was then stirred and further deaerated for two days by occasionally removing the vapors from the osmometer by expanding them into the outer evacuated system. To avoid possible splashing of the solution it was never opened directly to the pumps.

Analysis of the Solutions. Owing to changes in the concentration of unknown magnitude during the process of deaeration it was necessary to analyse the solution after removal from the osmometer following the determination of the osmotic pressure. Samples for analysis were removed without admitting air. It was thus possible to prepare a new dilution by distilling air-free water into the portion of the solution not removed. This was done by cooling the osmometer cell with a stream of ice water and slightly warming one of the air-free water bulbs. In this way it was found possible to make determinations on a whole series of dilutions with one salt without the annoyance of repeatedly having to deaerate the solution before use.

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[1] J. Am. Chem. Soc., **44**, 2468 (1922).

Electrical conductivity was chosen as a suitable means of determining the concentration of the small portion of dilute solution available for analysis.

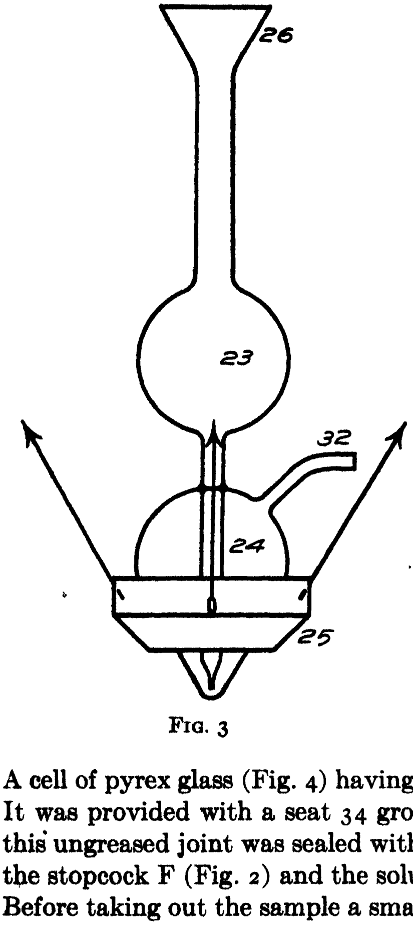

FIG. 3

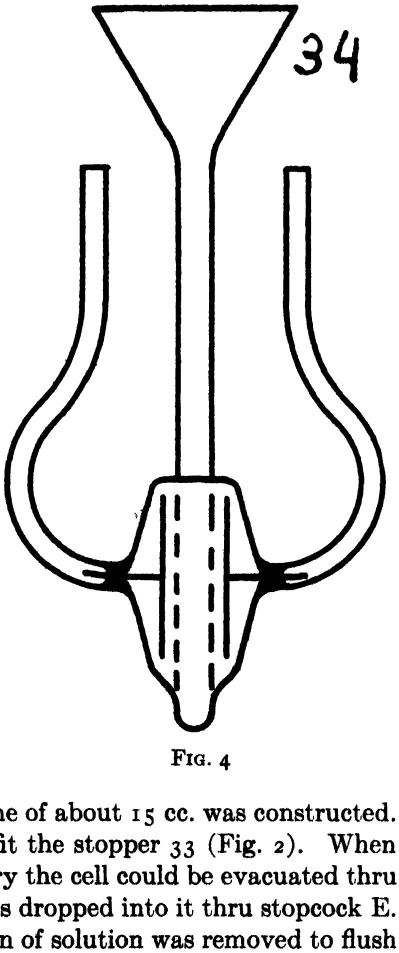

FIG. 4

A cell of pyrex glass (Fig. 4) having a volume of about 15 cc. was constructed. It was provided with a seat 34 ground to fit the stopper 33 (Fig. 2). When this ungreased joint was sealed with mercury the cell could be evacuated thru the stopcock F (Fig. 2) and the solution was dropped into it thru stopcock E. Before taking out the sample a small portion of solution was removed to flush out the stopcock E and the lower parts of the capillary tube above.

The conductivity of the sample was referred to a curve of conductivities for different standard solutions of the salt. These known solutions were measured in the same cell under conditions duplicating as nearly as possible the actual experimental procedure described above. At low concentrations the widest deviation of the standard conductivities from a regular curve was one and one-half per cent. All measurements of conductivity were corrected to the same temperature.

Measurements. Osmotic pressures were determined by estimating the tension exerted on the pure water under the disc at which distillation to or from the solution did not take place or, in other words, that tension at which there is no movement of the mercury meniscus in the capillary under the disc. By observing the rate of movement up or down of this meniscus when different tensions were applied, the required data were obtained. The tension was considered as being made up of the difference in height between the two mercury meniscuses added to the height of solution above the inner mercury meniscus in terms of water height all reduced to terms of height of mercury at zero degrees centigrade. All positions were read by a cathetometer on which they could be duplicated within 0.04 mm. The average of three readings was used for each position and the rate of movement was generally determined from five or six positions observed at about one hour intervals. Owing to the large surface the solution height was determined but once for each dilution as the amount of transfer of the solvent by distillation was extremely small. Because of occasional shifting of the entire apparatus it was necessary to observe, in connection with each set of readings, the height of a point of reference on the glass and make a correction when such shifts were noted. The largest sudden change in elevation of the entire apparatus observed was 0.2 mm. The probable cause of the shifting of the apparatus was that the thermostat tank, the bottom of which was made of copper, and was a meter in diameter, rested on a mat of ozite felt and may have been inclined to buckle.

The data needed in the determinations were height of the solution, height of the two mercury meniscuses, height of the reference point, time of each reading, and temperature of the bath. In case of a change in temperature greater than 0.002 degree the series was stopped and another not commenced until close regulation was restored.

The first experiments resulted in greater distillation from the disc than could be accounted for by the solutions in the osmometer. It was found that where the tube containing the spring suspension for the stirring device passed through the surface of the water in the bath there was a fog of condensed moisture. Though the room temperature was kept higher than that of the bath and the latter was covered with a lid, the evaporation from the surface of the water in the bath lowered the temperature sufficiently to cause distillation in the evacuated system. An air-tight housing over this part improved matters and results were more satisfactory but still too high. Later inspection showed that condensation was taking place even in some of the immersed tubes especially those nearest the central chimney. It was thought, despite fairly good stirring, that water cooled at the surface might stream down onto the apparatus and cause distillation. The entire bath was covered with liquid paraffin oil to stop surface evaporation and again the results showed noticeable improvement. There was still, however, reason to believe that the results were being influenced by non-uniformity of temperature perhaps from water pouring out of the top of the central chimney. Some improvement was noted after erection of a baffle to shield the apparatus from the currents of water directly from the chimney. Stirring downward was not feasible with the apparatus as constructed. A reconstruction of the apparatus placing trap V as closely as possible to the osmometer would be a desirable change suggested by this experience.

Results. As previously stated the first trials were unsuccessful. The determinations reported here were made after most of the changes related in

TABLE I

Solution 0.0020 molar KCl Temperature 26.429°C

Tension mm. mercury @ O C	Time, hours	Height of Meniscus millimeters	Rate of Distillation mm. per hour
A. 64.48	0	0	
	0.63	0.062	
	1.11	0.101	
	2.42	0.183	
	3.20	0.194	
	3.68	0.221	
	4.30	0.291	
	5.13	0.328	0.075
B. 82.40	0	0	
	0.87	0.014	
	1.42	0.075	
	1.97	0.088	
	4.48	0.114	
	4.89	0.120	
	5.70	0.175	
	6.23	0.190	0.028
C. 104.75	0	0	
	1.02	−0.024	
	1.92	−0.044	
	3.18	−0.116	
	3.88	−0.079	
	5.40	−0.119	
	6.63	−0.144	
	7.50	−0.171	−0.022
D. 122.94	0	0	
	1.90	−0.113	
	2.57	−0.112	
	3.12	−0.203	
	3.75	−0.214	
	4.65	−0.310	
	5.95	−0.330	
	6.23	−0.372	
	6.55	−0.394	−0.057

the preceding paragraph were carried out. As an illustration of the data and results, those data and results for the solution 0.0020 weight molar are given in Table I. The rates of distillation were calculated from the data by the method of moments. To show the relation of the individual coordinate points to the curves representing the calculated slopes and intercepts the results are shown graphically in Fig. 5. By reference to the scale it will be seen that the deviation of individual points from the curves is in very few cases greater than the limits of accuracy of the cathetometer readings.

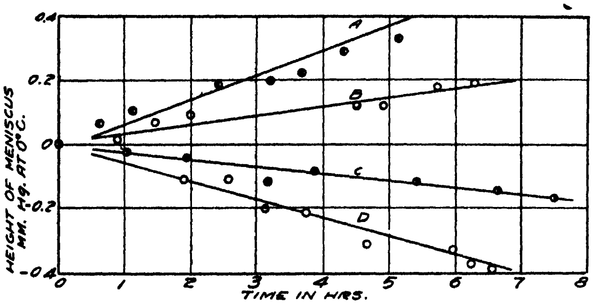

FIG. 5

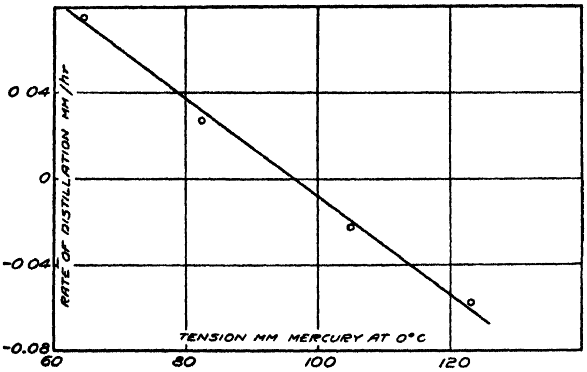

FIG. 6

Applying mathematical analysis to the rates and tensions given above, the calculated tension for zero rate of distillation, which should be the value of the osmotic pressure, is 96.5 mm. The graphic representation of these coordinate points and the curve drawn to the calculated slope and intercepts are shown in Fig. 6.

The results of five determinations on three solutions are shown in Table II. The ratio of the observed osmotic pressure to that calculated for a nondissociated nonhydrated solute is given along with the experimental results.

It will be noted, in Table II, that there is a tendency for the results to be higher than would be expected. Also they are somewhat inconsistent in the case of the second solution, which was run over a very extensive period of time without removal. The explanation is offered that these high values, which are

TABLE II

Concentration moles KCl/1000 grams water	Tension for zero rate of distillation	Ratio of tension of zero rate of calc. os. press. of nondissociated solute.
0.00504	187 mm.	1.986
0.00298	112.4 mm.	2.015
0.00298	111.5 mm.	2.005
0.00298	136.5 mm.	2.45
0.0020	96.5 mm.	2.58

the result of too great distillation from the disc and too little back into it, are caused by distillation taking place in other parts of the apparatus. As the vapor pressure, lowering for a 0.0020 molar solution due to solute, is around 0.001 mm., which is roughly that for a decrease of 0.001 degree in temperature, lack of uniformity of temperature throughout the apparatus seems to be the most probable cause of error.[1]

In conclusion the authors wish to express their appreciation to Professor J. C. W. Frazer and W. A. Patrick who suggested this research and under whose direction it was performed.

Summary: 1. The porous disc method for directly measuring osmotic pressure was applied to dilute solutions of potassium chloride with sufficient success to justify further work on it.

2. Errors in results were traceable to unequal temperatures within the apparatus and therefore suggested refinements in construction of the system.

3. Distillation was obtained at will in either direction with relation to the disc, which had not been found possible in preliminary work on this method.

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[1] The above explanation of the error is strengthened by results of later work done by Clara E. Miller using the same apparatus with pure water in the solution chamber. Operating in the usual way distillation was observed taking place from the disc even when slight tensions were applied. The water was tested for purity after removal and gave conductance measurements, checking those of the fresh conductivity water used. The only cause for distillation in this case would have been difference in temperature in different parts of the system.

THE ADSORPTION OF CHROMATE IONS BY COLLOIDAL ALUMINUM HYDROXIDE

BY BEN H. PETERSON AND KEITH H. STORKS

A great deal of research has been done on the adsorption and coagulating properties of electrolytes on colloidal suspensions of metallic hydroxides.[1] Many attempts have been made to formulate an equation which would express the relation between the amount of the coagulating ion adsorbed and the amount of the colloid of which the well known Freundlich isotherm is the most familiar.[2] The coagulation or precipitation values of different electrolytes on such colloidal systems have also been intensively studied in an attempt to find a relation between the valence of the coagulating ion, the mass of the colloid, and the effect of the associated ions. The actual mechanics of coagulation, that is, what actually happens to so reduce the stability of the system that the particles coalesce is rather difficult to picture. It has been shown,[3] that if the potential or charge on the colloidal particle is reduced below a certain value, the particles will adhere and coagulation take place. It hardly seems reasonable that this neutralization of the charge by adsorption of oppositely charged ions should be the same type of adsorption as that occurring *after* the coagulation of the system has taken place. If the mechanism of the adsorption which actually causes the coagulation is different from that which occurs on the surface of the coagulated particle, the adsorption isotherms as usually obtained may not have any significance in any theory attempting to explain the coagulating power of electrolytes.

A search of the literature did not reveal any data on adsorption at concentrations below that required for coagulation, although in many cases the isotherms are extrapolated to zero concentration of the electrolyte. If the above hypothesis be true, it follows that the adsorption isotherms obtained at concentrations less than and greater than that required for complete coagulation will show a break at that point where one type of adsorption ceases and the other begins. It was to test this hypothesis that the following experiments were performed.

Experimental

Aluminium hydroxide was precipitated from a purified sample of the chloride with ammonia. This was washed by decantation with distilled water until dispersion began. The partially purified precipitate was then dialyzed electrically using a potential drop of 80 volts until a moderately sensitive galvanometer placed in series gave only a slight deflection. This treatment yielded a product very free from adsorbed ions of any sort. The purified hydroxide was then dispersed in conductivity water and peptized with a few drops of hydrochloric acid. The positive suspension so prepared remained evenly dispersed during the three weeks it was allowed to stand before any samples were taken. Enough of the suspension for a complete run was transfered to a separate flask and 150 cc. samples transferred to each of twelve glass stoppered bottles. An equal volume of conductivity water was placed in an equal number of similar flasks to serve as blanks, and the suspensoid and water flasks paired. To each sample and corresponding blank was then added 50 cc. of a solution of potassium chromate of varying concentrations, each pair, suspensoid and blank, containing the same amount of electrolyte. The concentrations of the potassium chromate was so arranged that coagulation took place at about Flask No. 5. The entire set-up was allowed to stand three weeks to insure equilibrium. The residual chromate was determined by electrometric titration according to the method of Eppley and Vosburg[1] using a standard solution of ferrous sulphate. An aliquot part of the blank was titrated first and then an equal volume of the supernatant liquid in the cases where the colloid settled readily. Where coagulation was incomplete, the colloid was removed by ultra filtration using a special Berkfeld filter cone. The first few cc. of the filtrate so obtained was discarded in order to avoid any error on account of adsorption by the cone itself. Preliminary experiments showed no adsorption after the first few cc. had filtered through. The concentration of the chromate in the blank being known, the concentration of the residual solution from which the colloid had been removed could be calculated as:

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[1] Weiser: J. Phys. Chem., **28**, 232 (1924); Gann: Kolloidchem. Beihefte, **8**, 125 (1916); Weiser and Middleton: J. Phys. Chem., **24**, 639 (1920); Sen: J. Phys. Chem., **31**, 419, 525 (1927); Weiser: "The Hydrous Oxides" (1926); Ghosh and Dhar: "Studies on Adsorption," A series of researches published in J. Phys. Chem. during 1927-1929.

[2] Freundlich: "Kapillarchemie" (1922); Swain and Urquhart: J. Phys. Chem., **31**, 231-76 (1927).

[3] Powis: Z. physik. Chem., **89**, 91, 186 (1915).

$$\frac{\text{cc.FeSO}_4\text{ for residual soln.}}{\text{cc. FeSO}_4\text{ for blank}} \times \text{Conc. blank} = \text{Conc. Res. Soln.}$$

and from this value the amount of chromate adsorbed could be determined by difference. The mass of the colloid was determined gravimetrically from samples taken at the beginning of the run.

Experimental Results

The results are recorded in the Table as, millequivalents chromate left unadsorbed, "C", millequivalents adsorbed, "X", in columns I and II. In column III are given the values of X/M, and in column IV the values for log. "C". In column V are given the values of log. X/M. The star marks the sample containing the lowest concentration of chromate that coagulated completely. M, is the mass of the colloid.

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[1] Eppley and Vosburg: J. Am. Chem. Soc., **44**, 2148 (1922).

TABLE

Al_2O_3 per sample, "M", equals 0.09988 gms.

No.	"C"	"X"	X/M	log. "C"	log. X/M
1	0.23538	0.16407	1.64267	9.37157−10	0.21556
2	0.31472	0.16522	1.65419	9.49729−10	0.21859
3	0.39783	0.16210	1.62295	9.59970−10	0.21032
4	0.64844	0.15146	1.51642	9.81187−10	0.18081
5#	0.72941	0.15048	1.50661	9.86297−10	0.17800
6	0.78843	0.17145	1.71656	9.89676−10	0.23467
7	0.85551	0.18436	1.84581	9.93223−10	0.26618
8	0.93005	0.18981	1.90038	9.96851−10	0.27885
9	1.00516	0.19469	1.94924	0.00225	0.28986
10	1.18422	0.21561	2.15869	0.07343	0.33419
11	1.46059	0.23920	2.39847	0.16453	0.27929
12	1.71443	0.28532	2.85663	0.23411	0.45585

These results are plotted as X/M against C in Fig. 1 and as log. X/M × 10 against log. C × 10 in Fig. 2.

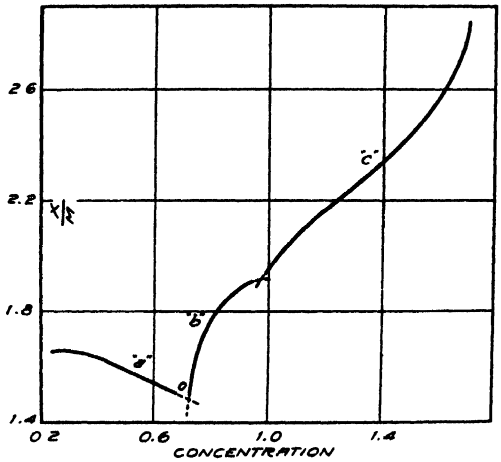

FIG. 1
Adsorption of Chromate Ions by Aluminum Hydroxide

Discussion of the Results

The curves shown in Figs. 1 and 2 show three distinct parts and have been labeled "a", "b" and "c". "a" represents the data obtained at concentrations below the coagulation value of the added electrolyte, terminating at point "o" which was the last sample to be coagulated. The section marked "b" was unexpected. The supernatant liquid was clear to the Tyndall beam, showing complete coagulation. Section "c" marks the isotherm as usually obtained. Two additional sets of data on suspensions similarly prepared, respectively three months and three years old showed the same type curves except the section "b" was more extended. These data are not recorded as the results are similar.

The hypothesis suggested in the introduction seems amply borne out by the results of these experiments, at least on colloid suspensions which are charged. If the mechanics of adsorption were the same in the uncoagulated and coagulated regions the curves would be continuous, i.e., there would be no sudden break. The break shown, so extreme as to even reverse the slope, indicates that the type of adsorption by the coagulated system is entirely different from the type of adsorption at concentrations below the coagulation values of the added electrolyte. An explanation for the section "b" is suggested. It is well known that the coagulation of a charged suspensoid takes place before the charge is completely neutralized. "b" may represent a combination of the neutralization adsorption represented by "a" and the surface adsorption as represented by "c".

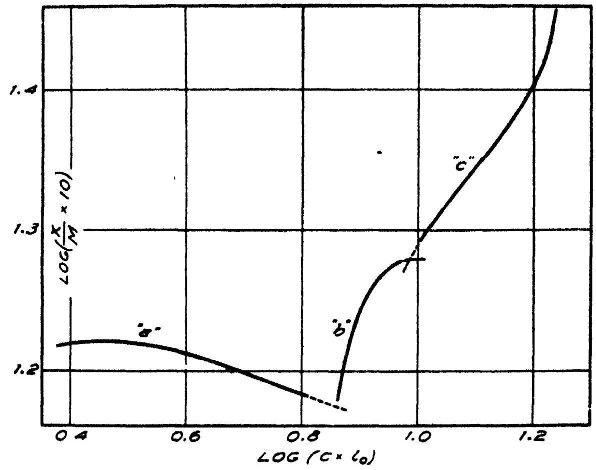

FIG. 2
Logarithm of the Adsorption Isotherms

Summary

1. The adsorption of potassium chromate by colloidal aluminum hydroxide has been determined at concentrations above and below that required for complete coagulation.

2. The results show three separate and distinct types of adsorption for which the explanation is offered: "a" represents a neutralization adsorption, that is, the neutralization of the positive charge on the suspensoid particle. "c" represents surface adsorption, not electrical in type and "b" represents a combination of these two types, "a" and "c".

3. The extrapolation of adsorption data to zero concentration of the adsorbed substance is not always justified.

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VARIATION OF EXTINCTION COEFFICIENT OF SOLUTIONS WITH TEMPERATURE. II

BY A. K. BHATTACHARYA AND N. R. DHAR

In a previous publication[1] from these laboratories it has been shown that the extinction coefficient of several coloured solutions and mixtures of different solutions markedly increase with rise in temperature.

In this communication we are submitting the results obtained with several other reacting mixtures.

For the measurement of the extinction coefficients, a Hilger-Nutting Spectrophotometer was used. To isolate any particular region of the spectrum for ease of comparison, a shuttered eyepiece was employed. The source of light was a 100 c.p. point-o-lite lamp working at 220 volts. Two similar, neutral-tint glass cells with optically-plane parallel ends were used, one for the solution whose extinction coefficient had to be observed and the other for an equal volume of distilled water so that the comparison might be made under identical conditions of original light intensity.

The time taken in actually reading the scale after the comparison of the two spectra did not exceed 45 seconds and precautions were taken to ensure constancy of temperature during this interval.

In the cases of reacting mixtures, titrations were carefully made to test that no appreciable change takes place at the lower and the higher temperatures during the very short time taken to read the scale on the photometer.

The following experimental results were obtained:—

1. *Neocyanin* (Kodak)—M/7176
Thickness of the cell—1 cm.
Spectral region—λ = 5490 Å

Temperature in °C.	Reading on the density scale	Extinction coefficient
10	0.84	0.84
40	0.86	0.86
70	0.90	0.90

2. *Ferric thiocyanate.*
10 c.c.—N/250 ferric chloride
10 c.c.—N/50 ammonium sulphocyanate
Spectral region λ = 5490 Å

10	0.72	0.72
40	0.73	0.73
70	0.75	0.75

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[1] J. Phys. Chem., **32**, 1834 (1928).

3. *Sodium cobaltinitrite*—M/80.8
Spectral region $\lambda = 5670$ Å

Temperature in °C.	Reading on the density scale	Extinction coefficient
10	0.85	0.85
40	0.86	0.86
70	0.88	0.88

4. *Sodium malonate and iodine.*
10 c.c.—N/2.69 sodium malonate
10 c.c.—N/100 iodine
Spectral region $\lambda = 5200$ Å

10	0.54	0.54
40	0.56	0.56
70	0.575	0.575

5. *Sodium tartrate and iodine.*
10 c.c.—N/2.42 sodium tartrate
10 c.c.—N/100 iodine
Spectral region $\lambda = 5490$ Å

10	0.48	0.48
40	0.50	0.50
70	0.515	0.515

6. *Citric acid and chromic acid.*
10 c.c.—6.75 N citric acid
10 c.c.—N/44.4 chromic acid
Spectral region $\lambda = 5000$ Å

10	0.51	0.51
40	0.52	0.52
70	0.535	0.535

7. *Lactic acid and chromic acid.*
10 c.c.—N/4.72 lactic acid
10 c.c.—N/44.4 chromic acid
Spectral region $\lambda = 4800$ Å

10	0.595	0.595
40	0.61	0.61
70	0.63	0.63

8. *Citric acid and potassium permanganate.*
10 c.c.—N/5 citric acid
5 c.c.—N/50 potassium permanganate
5 c.c.—N/69 manganous sulphate
Spectral region $\lambda = 5000$ Å

10	0.57	0.57
40	0.58	0.58
70	0.60	0.60

9. *Tartaric acid and potassium permanganate.*

5 c.c.—N/5.36 tartaric acid
10 c.c.—N/98.45 potassium permanganate
5 c.c.—N/69 manganous sulphate
Spectral region 4800 Å

Temperature in °C.	Reading on the density scale	Extinction coefficient
10	0.48	0.48
40	0.50	0.50
70	0.515	0.515

Discussion

In all the cases investigated above it may be observed that the extinction coefficients increase with increase in temperature. One thing however is to be noted that the increase in extinction coefficient is not marked unless the variation of temperature is great. We are of the opinion that there is increase in absorption for even small rise of temperature but this is too small to be observed.

These results can be explained from the point of view of the change of hydration of the solutes, at higher temperatures. The amount of hydration of a solute is likely to decrease on increase of temperature and this frequently leads to changes in the absorption. As the solvates become simpler on increase of temperature the absorption of light is likely to increase. It is generally found that the effect of increasing the temperature of the solution is the same as that of increasing the concentration of the solute. In both the cases there is an widening of the absorption bands—that is the absorption of light increases owing to the solvates becoming simpler (Compare H. C. Jones "The Nature of Solutions", page 331). Consequently the increased quantum yield on the increase of temperature of the reacting substances appears to be associated with the increase in the light absorption on increase of temperature.

Summary

1. The extinction coefficients of solutions of neocyanin, ferric thiocyanate, sodium cobaltinitrite, and mixtures of solutions of sodium malonate and iodine, sodium tartrate and iodine, citric acid and chromic acid, lactic acid and chromic acid, citric acid and potassium permanganate and tartaric acid and potassium permanganate appreciably increase with increase of temperature.

2. An explanation for this phenomenon has been put forward from the point of view of the change of hydration of the solutes at higher temperatures.

3. This increase in the extinction coefficient with temperature partly explains the frequent increase in the quantum yield with temperature.

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PHOTO-CHEMICAL DECOMPOSITION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTION IN PRESENCE OF SODIUM NITRO-PRUSSIDE. I

BY M. QURESHI

As is well known, an aqueous solution of hydrogen peroxide, free from dust particles and catalytic influences due to the surface of the containing vessel, is insensitive to the visible light. This is, however, not the case with a solution of hydrogen peroxide, to which a relatively small quantity of a mixture of potassium ferrocyanide and ferricyanide has been added. In the latter case, hydrogen peroxide suffers decomposition in the visible light with a brisk evolution of oxygen. This was discovered by Kistiakowsky,[1] who also found that the decomposition follows the unimolecular law and continues with undiminished velocity after the illumination ceases. According to the same author, an insolation of one minute in sunlight is sufficient to produce the maximum rate of decomposition. It has been further shown by Weigert[2] that the reaction takes place in the dark as well, when the solution of potassium ferrocyanide is first illuminated alone and afterwards added to the solution of hydrogen peroxide. Obviously, in the case studied by Kistiakowsky potassium ferrocyanide or ferricyanide, on illumination, gives rise to some catalyst, which remains effective in the dark. But the exact nature of this 'dark' catalyst is not yet definitely known. It may be of a colloidal nature, as suggested by Kistiakowsky, or it may be simply $Fe^{\cdots}$ ions, that are known to act catalytically in the thermal decomposition of hydrogen peroxide. There is a further possibility of both the catalysts appearing and working simultaneously. Any decision on this point must await the results of further experiments. In the meantime, it may be of interest to report another case of a similar nature, which throws some light on the nature of the catalyst, responsible for the after-effect in the photo-chemical decomposition of hydrogen peroxide.

While observing the decomposition of sodium nitro-prusside in the visible light, it occurred to the present writer to try the effect of nitro-prusside compounds on the photo-chemical decomposition of hydrogen peroxide. As the nitro-prusside compounds are decomposed by light with the formation of Prussian blue, it was thought very likely that an aqueous solution of hydrogen peroxide, to which a few drops of sodium nitro-prusside have been added, would be sensitive to the visible light, owing to the colloidal Prussian blue, formed as a result of the photo-chemical decomposition of the latter compound. These expectations came out to be true. An aqueous solution of hydrogen peroxide, to which a few drops of a freshly prepared solution of sodium nitro-prusside had been added, was fairly stable in the dark for long intervals of time. When the same solution was exposed in glass vessels to the light of a metal filament lamp or a quartz mercury vapour lamp, decomposition set in after a short time and continued with a brisk evolution of oxygen after the light was shut out. A few experiments are described below.

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[1] Z. physik. Chem., 35, 431 (1901).

[2] Ann. Physik, (4) 24, 261 (1907).

Experiment No. 1

One c.c. of a solution of sodium nitro-prusside (M/10), prepared in the dark, was added to one c.c. of 33% hydrogen peroxide, and the mixture made up to 100 c.c. by the addition of dust-free conductivity water. The process of mixing, which was carried out in a semi-dark room, did not take more than a minute. One portion of this mixture was transfered to a small, thoroughly cleaned, Erlenmeyer flask, placed in a thermostat, and exposed to the light of a quartz mercury lamp. The flask was closed by a cork, carrying a valve and an arrangement for pipetting out one c.c. of the mixture. The remaining portion of the mixture was transferred to a second flask, similar to the first, but painted black from outside for comparitive experiments in the dark. After an exposure of 10 minutes, the light was shut out and the course of the reaction followed in both the flasks by withdrawing one cc. of the mixture at noted intervals of time and titrating against potassium permanganate. The results are stated below. The values of the velocity constant ($K \times 10^5$), given in the last column of the table, have been calculated on the basis of the uni-molecular formula: $K = 1/t \log_{10}(a/(a-x))$.

TABLE I

(a) Rate of decomposition after exposure

Concentration of hydrogen peroxide = 0.1 molar approx).
Concentration of sodium nitro-prusside = 0.001 molar.
Time of exposure = 10 minutes.
Temperature = 30°.

Time (in minutes)	Permanganate titer (c.c.)	Velocity constant ($k \times 10^5$)
0	20.2	
19	19.3	104
38	18.4	109
69	16.7	136
117	14.7	115
(b) Rate of decomposition in the dark		
0	20.2	—
15	20.2	—
34	20.1	11
57	20.1	—
80	20.0	9

Experiment No. 2

In this experiment, the concentration of hydrogen peroxide was nearly half of that in the first experiment, but the time of exposure was increased to

15 minutes. Other conditions were the same as in the first experiment. For titrations, a burette, graduated to 1/50 c.c. with a certificate of N. P. L. was used.

TABLE II

(a) Rate of decomposition after exposure

Concentration of hydrogen peroxide = 0.05 molar (approx.)
Concentration of sodium nitro-prusside = 0.001 molar.
Time of exposure = 15 minutes.
Temperature = 30°.

Time (in minutes)	Permanganate titer (in c.c.)	Velocity constant ($k \times 10^6$)
0	8.58	—
21	8.02	139
45	7.26	180
65	6.85	126
91	6.32	134
	(b) Rate of decomposition in the dark	
0	9.28	—
51	9.20	7
76	9.14	11
141	9.02	9

Experiment No. 3

The mixture, exposed to light, appeared to possess a pale blue colour and showed Tyndall effect. The mixture, kept in the dark, however, neither developed blue colour nor showed Tyndall effect, but on standing for twenty-four hours deposited a precipitate of ferric hydroxide.

Experiment No. 4

On adding a few drops of a solution of nitro-prusside, that had been separately illuminated for half an hour, to an aqueous solution of hydrogen peroxide, evolution of oxygen took place in the dark. The course of this reaction was not followed quantitatively.

The above experiments, though preliminary in character, are sufficient to establish the following conclusions:

(1) An aqueous solution of hydrogen peroxide, to which a few drops of a solution of sodium nitro-prusside are added, is sensitive to the visible light.

(2) The decomposition of hydrogen peroxide, under the above conditions, continues after the illumination ceases. (photo-chemical after-effect).

(3) During the illumination, very probably colloidal Prussian blue is formed, which acts as a catalyst in the dark reaction.

Further experiments on the effect of the variation of intensity of illumination and temperature on this reaction are in progress and will be reported in due course.

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NOTE REGARDING THE COLLOIDAL NATURE OF CUPRAMMONIUM SOLUTION*

BY ALFRED J. STAMM[1]

The nature of the complex salts of copper and ammonia, and the reason for their intense blue color is one of considerable interest. Earlier investigations on the lowering of the freezing point,[2] vapor pressure depression,[3] distribution coefficient,[4] and change in viscosity[5] all showed that four ammonia radicals are combined with one copper to form the complex ion $Cu(NH_3)_4^{++}$. This relationship of copper to ammonia is not exact, however. According to Dawson,[6] dilution of the solution or decreasing the ammonia concentration relative to that of copper causes the equilibrium between the components to be displaced so that the ratio of combined ammonia to copper diminishes. Copper finally precipitates from solution as copper hydroxide.

Bhatnagar, Goyle, and Prasad[7] have recently shown that this deviation from the true stoichiometric relationship and the intense blue color of the solutions may be explained on the assumption that for all concentrations and proportions of ammonia and copper, part of the copper is colloidally dispersed as copper hydroxide. The amount of colloidal copper hydroxide present and its degree of dispersion, which affects the color of the solution, will vary with the relative concentrations of the constituents and the method of preparation. These investigators have further substantiated their theory by comparing four properties of copper hydroxide sols with those of cuprammonium solutions, namely the absorption spectra, cataphoresis, dialysis, and flocculation with electrolytes. In all cases the data indicate that the cuprammonium solutions contain some colloidally dispersed copper hydroxide.

The author had occasion, in connection with his study of the dispersion of cellulose in cuprammonium solvent,[8] to make a brief study of the colloidal nature of cuprammonium solvent itself, using the ultracentrifuge apparatus of Prof. The Svedberg.[9] In this study the concentration gradients existing in the sedimenting systems were determined by the new index of refraction method developed by Ole Lamm[10] in this laboratory.

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[2] Reychler: Bull. **3**, 13, 387 (1895).

[3] Gaus: Z. anorg Chem., **25**, 259 (1900).

[4] Dawson: J. Chem. Soc., **89**, 1668 (1906).

[5] Blanchard: J. Am. Chem. Soc., **26**, 1315 (1904).

[6] Dawson: J. Chem. Soc., **95**, 371 (1909).

[7] Bhatnager, Goyle and Prasad: Kolloid-Z., **44**, 79 (1928).

[8] Stamm: J. Am. Chem. Soc. **52** 3047, 3068 (1930).

[9] Svedberg, "Colloid Chemistry," pp. 146-167 (1928).

[10] Lamm: Z. physik. Chem., **138**, 313 (1928); **143**, 177 (1929).

The cuprammonium solution was prepared by drawing CO_2-free air slowly through a tall cylinder containing concentrated ammonia (sp. gr. 0.91) and strips of electrolytic copper foil for 6 hours. The copper concentration was determined by evaporation of 2 cc. portions, igniting and weighing as the oxide. The ammonia concentration was determined by titrating a diluted portion against 0.1 N HCl using methyl orange as an indicator. The stock solution contained 1.28 per cent copper and 22.0 per cent ammonia.

With the high-speed oil-turbine centrifuge a definite sedimentation of a polydisperse material was observed using the above stock cuprammonia solution. The sedimentation velocity ranged from 5×10^{-12} cm./sec. per cm./sec.^{2} to 10 to 100 times this value. The upper limit of the sedimentation velocity was not determined, as the author was primarily interested in the finer dispersion. This sedimentation value could have been definitely obtained by making measurements with the centrifuge operating at a lower speed.

If it is assumed that the colloidal material present is simple $Cu(OH)_2$, the density of which is 3.37, the particle size range can be calculated using Stokes' law of settling. This gives a particle size range from 6.5 mμ in diameter to more than 20.0 mμ. Unfortunately, the percentage of the total copper concentration that is colloidally dispersed can not be definitely determined without the knowledge of the relationship existing between the sol concentration and the refractive index. It is very likely less than 10 per cent of the total copper concentration, however.

Conclusions

It has been shown with the aid of the ultracentrifuge that cuprammonium solutions do contain a material in colloidal dispersion. This colloidal material is undoubtedly a copper hydroxide sol, according to the deductions drawn from the data of Bhatnagar, Goyle and Prasad.[7] This sol is polydisperse and contains particles ranging in diameter from 6.5 mμ to more than 20.0 mμ for the concentration investigated.

The author wishes to express his sincere thanks to Prof. Svedberg for the use of the ultracentrifuge equipment of this laboratory, and for the help which he always freely gave towards the carrying out of this research.

NEW BOOKS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. *By J. W. Mellor. Vol. X. 25 × 17 cm., pp. x + 958. London and New York: Longmans, Green and Co., 1930. Price: $20.00.* The tenth volume of this series deals with sulphur and selenium. The sulphur cycle is discussed on p. 9. "W. Lindgren has well emphasized the fact that in nature a large part of the sulphur is continually in movement, changing from sulphide to sulphate with local reversions to native sulphur, and from sulphate back to sulphide. He follows the cycle somewhat as follows: All active volcanoes give off enormous quantities of hydrogen sulphide some of which is oxidized to form sulphur dioxide and then the trioxide. The resulting sulphuric acid descends to the earth with rain to form sulphates by reacting with the basic rocks. A part of the hydrogen sulphide is reduced to native sulphur. All intrusions contain sulphur compounds part of which are fixed as metal sulphides—*e.g.* pyrites—which fill veins or impregnate adjacent rocks; or else as sulphates —*e.g.* barytes and anhydrite. Some of the silicated waters which come to the surface carry hydrogen sulphide in soln., and this gives rise to accumulations of native sulphur about the vent of springs.

"When the basic sulphide rocks are exposed at the surface, they are oxidized to soluble sulphates—*e.g.* iron, aluminum, magnesium, zinc, calcium, potassium, and sodium—which find their way to the sea. The less soluble sulphates—*e.g.* lead sulphate or the basic iron sulphates—linger behind. In the average river waters, sulphates are present in relatively large amounts, and enormous quantities are discharged into the ocean, so that the sulphates would predominate over the chlorides in the waters of the sea were it not for the continuous reduction of sulphates to sulphides along the littoral—particularly muddy shores rich in organic matter. Sulphur as iron sulphide is plentiful in shore deposits, and in some deep closed basins, like the Black Sea, similar reducing conditions obtain at the bottom, and the mud at the bottom is rich in iron sulphide.

"The evaporation of sea-water or lake-water in closed basins results in the deposition of calcium sulphate which forms nearly all the known beds of gypsum. When meteoric waters loaded with hydrocarbons act on calcium sulphate, the sulphate is reduced to sulphur. The sulphate may be similarly reduced by bacterial activity.

"The muds and silts, rich in iron sulphide, largely as marcasite, are compressed, raised, and folded by geological processes to form shales and sandstones. The sulphide is then attacked by oxidizing soln., converted into soluble sulphates and again carried back to the sea. The meteoric waters circulating at deeper levels, extract sulphates from uplifted sediments—limestone, slate, or silt—near the surface, and, lower down, the sulphides of hydrogen, iron, zinc, lead, copper, cadmium, cobalt, or nickel. The sulphides may be deposited elsewhere as in the zinc and lead sulphide deposits on the limestone of the Mississippi Valley."

At 600° calcium sulphite decomposes reversibly in two stages, p. 18. $4\ CaSO_3 = CaS + 3\ CaSO_4$ and $CaS + 3\ CaSO_4 = 4\ CaO + 4\ SO_2$. "The so-called plastic sulphur of Imbert, for use in agriculture, is not the viscous or plastic sulphur indicated in the next section but is a mixture of sulphur with 0.05 percent of ox-gall," p. 20. "Royer said that if a hot saturated solution of sulphur in turpentine be cooled rapidly, monoclinic sulphur is formed, and rhombic sulphur if cooled slowly," p. 24. "The Thomsen Chemical Co. prepared colloidal sulphur by grinding it with a colloid—say, 50 parts of sulphur, 5 of glue, and 50 of water; other protective colloids can be used—extract of soap bark, Irish moss, gum tragacanth, or gum arabic. The solution is not precipitated by sulphuric acid, and is used as an insecticide," p. 40. "The various methods for determining the molecular weight of sulphur show that, in all probability, this element, in the solid, liquid, or vaporous state (at a low temperature) has the complex molecule S_8," p. 59.

"According to J. Bohm, when flowers of sulphur are kneaded in ordinary water, the floating portions removed, and the immersed portions left in an open vessel covered with only a small quantity of water, sulphuric acid is produced, whereas if the flowers of sulphur are kept in spring-water, and the air is excluded, hydrogen sulphide is formed after a short time. Flowers of sulphur have been kept for a month or longer in well-water, daily changed, immediately produce hydrogen sulphide, and, after a few days, the water, if its volume does not greatly exceed that of the flowers of sulphur, gives with a solution of a lead salt, a black precipitate, and with barium chloride, a moderate turbidity. In sealed tubes, with flowers of sulphur not very well adapted for the production of hydrogen sulphide, the formation of the gas is permanently hindered by the presence of air, even in small quantity. The same effect is produced by any acid or by phenol; carbon disulphide prevents the action only when the flowers of sulphur have been well mixed with a few drops of it. Flowers of sulphur thus treated, and then freed from the admixed substance, also those which have been boiled or frozen for some days, do not recover the power of immediately producing hydrogen sulphide till they have digested for some time in spring-water, daily renewed. In distilled water, no hydrogen sulphide is evolved, and even flowers of sulphur highly capable of generating this gas, lose the power of immediately producing it, even in spring-water, if they have been washed with pure water and kept for some time. In distilled water mixed with a little chalk, much less hydrogen sulphide is formed, than under similar conditions in spring-water, and a large quantity of chalk prevents the formation of the gas, even under circumstances otherwise favourable. The same is true in a still higher degree for gypsum, and for a considerable quantity of charcoal-powder freed from air by boiling. In the latter case the liquid, which in most cases is faintly alkaline, is strongly clouded by barium chloride. Hydrogen sulphide is also formed on boiling sulphur in water," p. 91.

"Sulphur has no action on the skin, but some of it may be converted into hydrogen sulphide which acts as a mild vascular stimulant and with some persons produces eczema; some sulphur may be converted into sulphurous and sulphuric acid which act as irritants. If taken internally, most of it passes out in the faeces unaltered; but a small proportion is converted in the intestine into hydrogen sulphide and other sulphides. These have a mild laxative effect, which is sometimes accompanied by a flatus of hydrogen sulphide which makes sulphur an undesirable laxative. Excessive amounts of sulphides and hydrogen sulphide may produce symptoms of asphyxia, and paralyze the nervous and muscular systems. . . . According to L. C. Maillard, colloidal sulphur, prepared by the interaction of hydrogen sulphide and sulphur dioxide, is completely and rapidly absorbed by rabbits when introduced into the aesophagus. Within twenty four hours, somewhat less than half is eliminated with the urine as mineral sulphates, and a portion in the form of organic sulphates. The normal amount of the latter is increased by 5-13 per cent. after the ingestion of sulphur, but the proportion falls below normal when this is withdrawn from the diet. About half of the sulphur is excreted in an incompletely oxidized condition, probably in organic combination, since no sulphur, hydrogen sulphide, or sulphur dioxide is formed on treating the urine with acid. It may be supposed that substances are formed by the conjugation of compounds of the type $R.SO_2.OH$ with phenols, and that more highly oxidized compounds escape combination in this way. L. Sabbatani showed that when the hydrosol is injected subcutaneously, hydrogen sulphide is formed only very slowly. After interperitoneal injection it is formed more rapidly, but yet not sufficiently quickly for it to be detectable in the expired air. When injected intravenously, it is readily formed, and for this reason the hydrosol of sulphur is very toxic. As the sulphur aggregates become larger, the toxicity diminishes. The dog can tolerate relatively large doses when the sulphur is introduced into the stomach. With the larger doses vomiting occurs, and the animal rapidly recovers. The sulphur is more toxic under the same conditions in rabbits, as these animals cannot vomit. A little more than 0.1 grm. per kilo. of body-weight can produce death. This dose can be well tolerated when introduced intraperitoneally or subcutaneously, although larger doses can act toxically. When given intravenously, doses of 0.0065-0.0203 grm. are toxic, the toxicity depending on the rate at which the sulphur is introduced," p. 104.

T. M. Lowry points out that optical activity occurs in a trisubstituted sulphonium ion, although it does not exist in the analogous molecule of ammonia. "No analogous difference exists between the electronic formula for the two groups since in each case the central atom carries three pairs of shared electrons with one 'lone pair' to complete the octet. The contrast is, therefore probably due to the existence in the nitrogen-compound of a mobility of atomic or molecular structure, similar to that which makes it easy to form a double or triple bond between elements of the first short period, whereas this is difficult or impossible in elements of the later periods," p. 111.

The reaction between sulphur dioxide and hydrogen sulphide occurs practically completely at the glass surface which therefore acts as a contact catalyst; each of the reacting gases being activated when adsorbed and the reaction taking place between the activated molecules. Quam said that dry sulphur dioxide reacts vigorously with liquid hydrogen sulphide. H. B. Baker found that liquid alcohol and liquid sulphur dioxide can liberate sulphur from the dried mixed gases, whereas carbon tetrachloride is inert. "According to D. Klein, immediate action is produced by water, ethyl alchool, *iso*butyl alcohol, *iso*amyl alcohol, acetone, propyl acetate, benzaldehyde, and carvone. A slower decomposition occurs with methyl ethyl ketone, acetonitrile, propionitrile, valeronitrile, phenylacetonitrile, methyl benzoate, *iso*butyl acetate, and ethyl ether. On the other hand, carbon disulphide, acetyl chloride, benzoyl chloride, ethyl chloride, and carbon tetrachloride are quite inert. There appears to be no connection between the dielectric capacity or association factor of a liquid and its activity as a catalyst in this reaction. Many of the active liquids are known to form compounds with hydrogen sulphide, notably the nitriles, the aldehydes, and carvone. E. Matthews also found that in order to bring about the decomposition of a mixture of sulphur dioxide and hydrogen sulphide in either the gaseous or the liquid state, the addition of a third substance in the liquid phase is necessary. There is no rigid relationship between the values of the dielectric constants of substances and their chemical activity as measured by their ability to bring about the interaction of hydrogen sulphide and sulphur dioxide. Hydrogen sulphide and sulphur dioxide when in liquid state do not react vigorously. The activity of a substance in causing decomposition is dependent on the solubility of the two gases in the substance when liquid, or on the solubility of the solids in the liquid mixture of the two gases," p. 135.

"The aqueous solution of hydrogen sulphide and the gas are poisonous, but less poisonous than chlorine or bromine. Toward the end of the eighteenth century a number of accidental deaths occurred in Paris due to the gases from the sewers; and in 1785 M. Hallé reported on the conditions but did not recognize hydrogen sulphide as the cause of the poisoning. . . . . Mitchell and Davenport say that hydrogen sulphide is one of the most toxic gases, and is comparable to hydrogen cyanide with respect to rapidity of action and concentration producing death. The action depends upon the concentration—0.005 percent is sufficient to produce poisoning, while a continued exposure to a concentration of 0.02 percent during several days may produce death," p. 145. In this last respect it is not like hydrogen cyanide the effect of which is not cumulative.

Mellor calls Schützenberger's acid hyposulphurous instead of hydrosulphurous acid, p. 167. "The effect of passing from weakly acid to strongly acid solution is to lower the oxidation potential of ferric-ferrous chlorides and phosphates, and to raise that of sulphur dioxide. The oxidation potential of cupric-cuprous chloride is actually raised by an increase in potential up to about 6.5 N, after which it decreases," p. 202.

"F. C. Calvert found that a solution 1:1000 does not affect protoplasmic life or fungi. According to M. Ogata, sulphurous acid under all conditions is a powerful poison; a solution with only 0.04 per cent. produced, after a few hours, a dyspnoea and darkening at the cuticle. The injurious action is mainly on the blood where the absorbed acid is converted into sulphuric acid. This action was not observed with sulphites. Diluted blood, decolorized with sulphur dioxide, shows no spectral absorption bands. H. Kionka found that relatively small proportions of sulphur dioxide in the atmosphere proved fatal. Doses of 0.02-0.04 grm. of sodium sulphite injected into frogs paralyze the heart, the central, and to some extent the peripheral nervous system. Dogs fed on the salt, or on food preserved by its use, suffer from injuries to various organs, especially the lungs and kidneys; there is local irritation of the stomach, and a fall of blood pressure, and haemorrhages tend to occur. The use of the salt as a preservative is most reprehensible. . . . The trees in an atmosphere containing sulphur dioxide, as occurs, for instance, in the neighborhood of smelting works, suffer severely. According to J. Schroder, the coniferae suffer more injury than ordinary foliaged trees. The number of stomata on the leaves bears no proportion to the amount of gas taken up. The sulphur dioxide disturbs the normal relation between absorption and transpiration of water, and the water taken up goes to the veins, and is not transmitted further. A decrease in the amount of the gas caused less disturbance in the amount of transpired water, though no simple proportion between the amount of the gas and of decrease was indicated. The amount of sulphur dioxide taken up by the leaves in the dark and with a lower temperature and moister air, is smaller and its injurious effects much lews marked than in the light and with higher temperature and moister air; therefore the same amount of sulphur dioxide in the air is much less injurious to plants during the night than in the daytime. The amount of sulphur dioxide absorbed by pine-leaves is smaller than that absorbed by trees with ordinary foliage for equal surfaces, and as its effect on transpiration is less in the case of the pine, the cause of the greater injury to pine trees in nature must be due to the longer duration of the leaves, whereby the injury accumulates in them, whilst in trees with annual leaves the hurt to one year's foliage would have only an indirect influence on that of the following year. The alder, sycamore, ash, and especially maple, best withstand the action of smoke containing sulphur dioxide; next the pines suffer more than other trees, owing to the fact that, although their sensitiveness at first is less than that of other trees, their power of restoring lost leaves is much less," p. 242.

When a sodium mercuric sulphite solution is heated, there is a separation of mercury which first appears as a bright rolling cloud, suggesting a precipitate of great volume, an effect apparently due to metallic reflection of light. This cloud then melts away, leaving a relatively minute, very dark grey deposit of mercury at the bottom of the vessel; the bright cloud becomes, so to speak, a rain of mercury, p. 297.

Reference is made, p. 338, to the use of vanadium pentoxide as a catalyst in the contact sulphuric acid process; but the author says that platinum is the only catalyst of technical importance, p. 339.

"Sulphuric acid is poisonous to man, and a fatal case of the poisoning of an adult by 3.8 grms. of acid was reported by R. Christison, and this is the smallest lethal dose on record. When externally applied, the concentrated acid may produce phenomena resembling scalds or burns; the destruction of the tissue may not be deep seated if the acid is quickly washed off. The skin is at first coloured white, and at a later period brown, and part may appear as if it had been dissolved. When administered internally, there is immediate and great suffering; the tongue and throat swell and inflame so that saliva cannot be swallowed. The acid attacks the mucous membrane of the gullet, and stomach. There may be excessive vomiting and retching. Pieces of mucous membrane may be expelled. The bowels are usually constipated, and the urine contains an excess of sulphates and often albumen with hyaline casts of unriniferous tubes. The pulse is small, the breathing slow, the extremities may be affected with convulsions and cramps, and death may follow in 24-36 hrs., or be more protracted and painful. In bad cases, the sulphuric acid may dissolve the stomach and pass into the peritoneium producing effects like a penetrating wound in the abdomen. In chromic poisoning by small doses W. Starkoff showed that it acts as a specific poison on the blood. R. Kobert mentioned that drunkards addicted to Schnapps may show symptoms of chronic poisoning because this liquor is acidified with sulphuric acid to give it a sharp taste," p. 440.

"According to H. Schulze, camphor readily absorbs sulphur dioxide and thereby liquefies, and the absorbed gas escapes when the liquid is exposed to air. Chlorine gas has no action on camphor, but is greedily absorbed by the above liquid until saturated, and a solution of camphor in sulphuryl chloride is formed, which can be easily separated and obtained pure by distillation. This action cannot be due to the mere condensation of the sulphurous anhydride and its action in the liquid state on the chlorine for these two gases do not combine even when condensed and cooled to −20°; but, on the other hand, in presence of camphor the reaction takes place even at −20°. Sulphurous anhydride combines in large proportion with and liquefies glacial acetic and formic acids; these acids are scarcely attacked by chlorine if sunlight is excluded, but the sulphurous compounds greedily absorb chlorine with formation of sulphuryl chloride, the acetic and formic acids remaining almost unacted on; thus their mode of action seems to resemble that of camphor. Alcohol and acetone also absorb quantities of sulphur dioxide; chlorine passed through these liquids acts on the alcohol and acetone, and in proportion as this proceeds the sulphurous anhydride escapes without being acted on. Other absorbents of sulphurous anhydride are sulphuryl chloride itself, and liquid sulphur trioxide. Chlorine passed into the latter solution does not yield a trace of sulphuryl chloride, no more than it does with the former. Turpentine absorbs sulphur dioxide, but it does not effect the union of this body with chlorine. Carbon bisulphide and chloroform absorb chlorine, but the solution is not acted on by sulphur dioxide. It cannot be supposed that the action of camphor, or acetic or formic acids, is due to their combining momentarily with chlorine, and then passing it over to the sulphur dioxide *in statu nascendi,* for the first two undergo substitution to a slight extent only and the last is completely decomposed into carbonic anhydride and hydrochloric acid," p. 668.

The author does not commit himself on the question whether perselenates have or have not been formed electrolytically, p. 852; on the question whether one has $SeO_2.2HCl$ or $SeOCl_2.H_2O$, p. 913.

Wilder D. Bancroft

Introduction to Physiological Chemistry. *By Meyer Bodansky. Second edition, rewritten and reset. 23 × 15 cm; pp. ix + 542. New York: John Wiley and Sons, 1930. Price: $4.00.* The first edition was reviewed four years ago (**31**, 1106). In this new edition two chapters have been added, one dealing with the composition of foodstuffs and the other devoted to a brief consideration of the composition of milk and of certain tissues, including bone, cartilage and muscle.

"The lactones of the sugar acids are relatively stable and some have been prepared in crystalline form. Levene is of the opinion that in a solution of sugar acids, all theoretically possible lactones are formed. In a freshly prepared solution the unstable lactones are said to predominate; but, after a short time, only the stable forms are present in measurable quantities," p. 45. "Until recently it was generaly believed that the sugar in animal nucleic acid (thymonucleic acid) was an hexose; but, according to recent observations, it is desoxyaldopentose, namely, *d*-2-ribodesose," p. 56. "Mannose is the constituent sugar of the mannans, a group of polysaccharides widely distributed in plants, but which are especially abundant in the endosperm of the seed of the tagua palm. Recently, Levene and Mori reported mannose to be a constituent of ovomucoid, a conjugated protein which occurs in egg white," p. 57.

"Arachidonic acid, and possibly tetracosapentenoic acid, $C_{24}H_{38}O_2$, are said to occur in the brain, where the highly unsaturated fatty acids seem to be present in greater proportion than in other tissues," p. 74.

"The synthesis of proteins in the plant can take place in the dark, provided there is an adequate supply of carbohydrate and potassium," p. 99. Vickery and Osborn give nine reasons for believing that the peptide binding, .C(:O).NH., is the principle linkage existing between the amino acids in the protein molecule. The ninth reason, p. 101, is as follows: "Pepsin alone liberates as a rule about 20 percent of the total amount of amino nitrogen which can be obtained by the complete hydrolysis of a protein. Erepsin acting on a peptic digest can liberate as much as 70 percent more. Since there is every reason to believe that the latter enzyme acts only upon peptide bonds, it is obvious that by far the greater part of the total possible amino nitrogen of a protein has its origin in such bonds."

The author calls attention to the fact, p. 102, that "certain facts seem to point to the possibility that the protein molecule is not merely a single large polypeptide. This type of structure is believed to be inconsistent with the changes which protein undergoes in the process of denaturation by alcohol or heat. Nor is it possible to explain the insolubility in water of many proteins on the basis of a polypeptide structure. [Neither of these objections seems to have any value.] An even greater obstacle in accepting the peptide bond as being the sole link between amino acids is the behavior of pepsin towards polypeptides. Pepsin does not act on polypeptides, nor for that matter on any synthetic products formed from amino acids. In fact, it is not known which bonds in the protein molecule are attacked by this enzyme."

"Rawlins and Schmidt have titrated casein, fibrin, gelatin, and edestin with certain basic dyes, methylene blue, safranine Y, and induline scarlet and found that the union between protein and basic dye occurred in stoichiometric proportions," p. 110. People have also titrated lead acetate with sodium eosinate and found stoichiometric relations; but they did not have lead eosinate after all. The experiments of Bancroft and Barnett with ammonia and hydrogen chloride gas on proteins are mentioned without comment, p. 114. The purification of urease by Sumner and of pepsin by Northrop are mentioned, p. 126. "Attempts to correlate our knowledge of enzyme action have resulted in the formulation of two main rival theories. Bayliss has advanced a colloid chemical point of view. According to this, the substances which react are first absorbed on the surface of the enzyme particles. The chemical reaction then takes place at the interface. Though this chemical reaction may be subject to the law of mass action,—namely, that the rate of reaction at any moment is proportional to the concentration at the moment of the reacting substances, still it is the adsorbed portion of the substances which is the controlling factor.

"The Michaelis school, on the other hand, has assumed that enzyme and substrate unite chemically, as ions would, to form an intermediate substance and that the rate of reaction is proportional to the concentration of this intermediate enzyme-substrate compound. These assumptions imply that the substances involved act as if they were in homogeneous solution. A good exposition of Michaelis' theory and the work upon which it is based is given by Waldschmidt-Leitz," p. 126.

"Proteins, therefore, are foods when absorbed in the usual way as amino acids, and poisons when introduced directly into the blood. One of the most violent poisons known is ricin, the protein of the castor bean. The injection of a protein that is foreign to the tissues of an animal results in the excretion of most of it in the urine. If the injection is repeated a few days later, no ill effects ensue. Continued injection of small amounts of a given protein at short intervals establishes an immunity for that protein, due, it is believed, to the formation of a precipitin, in the presence of which the foreign protein is precipitated. If, however, the second injection is administered several weeks after the first, severe shock is induced. This phenomenon is termed *anaphylaxis* and has among its symptoms a marked fall in blood pressure and a reduction in the coagulability of the blood. According to some investigators anaphylactic shock and peptone shock are essentially the same, the former being due to the development in the sensitized animal of an enzyme capable of converting the foreign protein in question into proteoses and peptones. 'Serum-sickness' frequently occurs in individuals sensitized against horse-serum proteins, and develops after the injection of antitoxins, such as diphtheria antitoxin. Under these conditions typical anaphylactic shock may occur and may terminate fatally," p. 181.

"The protein content of the plasma amounts to about 7 percent in man. The proteins may be separated into several fractions, the method most commonly employed consisting in salting out the fractions with varying concentrations of certain inorganic salts. From the work of Howe and others, it appears that the precipitation of the protein fractions occurs with some regularity. Thus, in a 0.75 molar solution of sodium sulfate, fibrinogen separates out. Euglobulin is salted out in a 1.00 molar solution. In a solution that is 1.25 molar, fibrinogen, euglobulin, and the so-called pseudoglobulin I are precipitated. All the globulins are separated from the albumins in a 1.50 molar solution, the last of the globulin fractions being pseudoglobulin II. Similarly various albumin fractions are precipitated in concentrations above 1.50 molar. While Howe recognizes the probability that the precipitates of protein may not be chemical identities, he has nevertheless suggested the grouping of the albumins into five fractions: V, VI, VII, VIII, and IX, which are precipitated in 1.75, 2.00, 2.25, 2.50, and 2.75 molar solutions of sodium sulfate, respectively," p. 216.

"In one particular is there less confusion than formerly, and this is with regard to the origin of blood sugar from liver glycogen, but not from muscle glycogen. The process glycogen ⇄ glucose occurs in the liver and the sugar thus formed is liberated into the systematic circulation. Reconversion of this sugar into glycogen occurs in the muscles, where, as we have seen, the reaction glycogen ⇄ lactic acid takes place. The lactic acid formed during muscular contraction is for the most part reconverted into glycogen during the recovery phase, but a small amount of lactic acid escapes into the blood. Even in a state of rest, the blood contains lactic acid, which has been estimated to vary between 5 and 20 mg. per 100 cc. of blood. In moderate exercise the blood lactic acid increases. For example, walking at a rate of 3.5 miles per hour was found by Hill, Long and Lupton to cause the lactic acid content of the blood to increase from 20.9 mg. (the concentration before the period of exercise) to 36.6 mg. per 100 cc. Somewhat more strenuous exercise, namely walking at the rate of 4.1 miles per hour, produced an increase of from 21.4 mg., the initial value, to 58.9 mg. per 100 cc.," p. 284.

"Now, what we are primarily interested in here is the fate of the lactic acid which escapes into the blood, for, it is seen, this occurs to some extent even in the resting condition and is much increased during exercise. A small portion of the lactic acid is excreted in the urine and the amount lost in this way may be considerable during violent exercise, but the larger proportion is returned to the liver, there to be resynthesized into glycogen. Thus, as Cori and Cori have pointed out, a sugar molecule can go through a complete cycle in the body; it can in turn be liver glycogen, blood sugar, muscle glycogen, blood lactic acid, and again liver glycogen. An abundance of evidence has accumulated in support of this idea but only a small portion of the literature can be referred to here. For example, the question as to whether muscle glycogen is converted directly into glucose has been virtually settled. When the liver is removed, the blood sugar rapidly falls to very low levels, as shown by the work of Bollman, Mann and Magath. As the muscle contains considerable amounts of glycogen and as this does not prevent the hypoglycemia and does not disappear to any great extent, it is concluded that muscle glycogen is not readily converted into glucose.

"It is well known that epinephrin, ether anesthesia and asphyxia produce hyperglycemia. But, as has been shown by Soskin, if the abdominal viscera, including the liver, are removed, hyperglycemia does not develop under these conditions despite the fact that there is glycogen in the muscles.

"There remains to be considered some of the evidence for the transformation of lactic acid into glycogen in the liver. It is to be supposed that in severe liver damage, as in phosphorus poisoning, the liver would lose its ability to convert lactic acid into glycogen and that there would be an increased excretion of lactic acid in the urine. This is actually the case. More direct evidence is that of Parnas and Baer, who observed glycogen synthesis in the turtle liver, perfused with sodium lactate. Similar observations have been made by many others, although occasionally negative results have been reported. Abramson, Eggleston and Eggleston were unable to demonstrate the synthesis of glycogen in the liver from racemic sodium lactate in dogs under amytal anesthesia. On the other hand, Izume and Lewis observed glycogen deposition in the liver of fasting rabbits injected subcutaneously with sodium lactate, and more recently Cori and Cori, working with rats, found that if sodium *d*-lactate is fed by mouth or injected subcutaneously, glycogen is deposited in the liver. Sodium *l*-lactate, though absorbed from the intestine at the same rate as the *d*-isomer, hardly formed any liver glycogen. Cori and Cori state that of the *d*-lactate absorbed in three hours, 40-95 per cent was retained as liver glycogen and none was excreted in the urine, whereas 30 per cent of the *l*-lactate absorbed was recovered in the urine," p. 285.

"Holmes, Gerard and Solomon have shown that during rest in oxygen there is no change in the glycogen or lactic acid content of nerve. The 'free sugar,' on the contrary, decreases in amount with time. In rabbit nerves, at 37°C., the decrease is 36 mg. percent for the first hour and progressively less during later periods. In bullfrog nerves, at 22° C., the rate of 'free sugar' is constant for at least nine hours at 6 mg. percent, per hour. This is 50 percent more than can be oxidized by all the oxygen used by the nerve at rest. The fate of this sugar is unknown," p. 287.

Wilder D. Bancroft

Colloids. *By H, R. Kruyt. Translated by H. S. van Klooster. Second edition. 23 × 15 cm; pp. xi + 286. New York: John Wiley and Sons, 1930. Price: $3.50.* The first edition of this book appeared in 1927 and was reviewed (32, 316). The general plan is the same as the earlier edition, the revision having been limited to bringing the text up to the level of 1929. General headings of the sections are: general introduction, suspensoids, emulsoids, and special cases. Practically the entire book is devoted to aqueous suspensoids and emulsoids, the special cases being intermediate between these. There is therefore little to be found concerning systems in which liquids other than water, solids, or gases are the dispersion media. The whole problem of catalysis with its large commercial importance is omitted, as are also any references to such colloidal systems as foams, fogs, smokes, etc.

"Color is indeed a characteristic property of colloidal solutions. A dilute solution of ferric chloride is slightly yellow; when this solution is poured into boiling water, a colloidal solution of Fe_2O_3 is formed by hydrolysis, and thus with the same amount of iron, a deep red liquid is produced. Sols show strong coloration, and have more pronounced absorption bands than the corresponding molecularly or ionically dispersed systems.

"It is obvious that some relation exists between the size of the dispersed particle and the light absorption. The phenomenon of the change in color from red to blue, exhibited by a gold sol at the beginning of coagulation, has been known for years and has led to the search for a direct connection between light absorption and size of particle. This relation, however, can evidently be simple only when the shape of the particles is comparable, i.e., when we are dealing, for instance, with spherical particles of different radius. When a sol flocculates, however, the particles coagulate in the form of warty lumps so that not merely the radius but also the shape of the surface and the density of the particle taken as a whole are changed. This is no doubt an important factor in the case of the gold sol, because we are not at all sure that a highly dispersed gold sol is red and a slightly disperse sol blue. On the contrary, it is quite possible to prepare a blue gold sol which is more dispersed than one that looks red.

"Zsigmondy found that, in general, a sol consisting exclusively of primary particles appears red, while the agglomeration of such spherical particles to multiple particles causes a change to blue. All blue gold sols, therefore, have undergone coagulation to some extent," p. 132. The discussion of ultrafiltration contains these paragraphs:

"This forced dialysis, or osmosis (depending on the point of view), is sometimes useful for preparatory purposes. On page 112 we saw, for instance, that such a separation of the intermicellar liquid serves a definite purpose. It has been wrongly assumed, however, that ultrafiltration in itself affords a means of determining the size of the particles. By choosing different concentrations of collodion solution, membranes of different degrees of permeability are obtained, and this has been considered to be due to different degrees of porosity of the membranes, the latter acting as sieves.

"This assumption, however, appears to be largely incorrect. Filter and membrane action is only to a limited extent comparable with the action of a sieve, and is much more dependent on the adsorption at the capillary wall than on the mechanical dimensions of the pores. For instance, a positively charged colloid cannot be filtered through a negatively charged filter paper, when the latter is rather thick; a negative sol, however, passes through easily. This question will be reconsidered later. Bechhold has reported a close connection between the concentration of his membranes and the size of the particles held back by them, but this fact in itself does not prove anything regarding the sieve mechanism of the ultrafilter. It is also possible that the adsorbability runs parallel with the particle size. If we could consider substances that are comparable as regards their adsorbability and their electro-adsorbability, a direct connection between the size of the particles and the nature of the ultrafilters might add something to our knowledge of the size of the particles; but a comparison of completely dissimilar substances, on the basis of their behavior toward ultrafilters, does not permit any conclusion regarding the size of the particles." p. 159.

"There is, however, a special reason which has led many investigators to look upon emulsoids as molecularly dispersed systems, more particularly, as electrolyte solutions; this is the fact that a great many properties of protein solutions may be explained by considering these solutions as systems of *amphoteric electrolytes*. This train of thought will be fully considered in the next chapter and shown to be incorrect. It may be pointed out at this place that a discussion of emulsoids in terms of ionically dispersed systems must necessarily conflict with typically colloidal properties of these systems. We do not know any electrolyte solutions that scatter light in a corresponding manner (Tyndall effect), show no lowering of the freezing point or rise of the boiling point, and produce, for such minute concentrations, such exceedingly viscous solutions. The fact that protein solutions do not pass through dialysis membranes might possibly be explained on the basis of a large number of atoms in the molecule, but the other properties mentioned here cannot be connected with large molecular weight without leaving the domain of general chemical experience," p. 190.

In the preface to the first edition, reprinted in the second is found: "As is indicated on the title page, this book is intended for use as a textbook. In other words, it is the author's purpose to offer a main line of orientation to students who wish to become acquainted with the general trend of Colloid Chemistry or who desire to undertake research in this particular branch of Chemistry." Any textbook must necessarily be limited in the choice of subjects and in the exhaustiveness of their treatment. This one appears to bear out the statement: "Completeness has nowhere been the aim, but the arguments are constantly advanced." If one is content to accept the limitations chosen by Kruyt, one finds that this is a satisfactory textbook for the material covered. It is clear, readable, well supplied with references to the literature, and utilizes repeatedly the device of teaching, by an illustration or compact word-picture, the state of things as Kruyt believes them to exist in colloidal systems. For many readers this making of pictures after the argument has substantiated the picture proves a valuable aid in the retention of the concept proposed.

Herbert L. Davis

The Fundamentals of Chemical Thermodynamics. *By J. A. V. Butler. 19 × 13 cm; pp. xi + 207. London: Macmillan and Co., Limited, 1928.* In the preface the author says: "I have tried to present the subject in a logically precise yet simple form, having in mind not only the student who intends to specialize in Physical Chemistry, but also that class of chemistry students which has only a very moderate knowledge of mathematics and little sympathy with mathematical methods.... The present volume, containing the 'elementary theory,' is based mainly on cyclic processes. A second part is in preparation, which will deal with the more advanced parts of the subject, mainly on the basis of thermodynamic functions."

The subject is treated under the general heads: the first law of thermodynamics; the second law of thermodynamics; changes of state; solutions, homogeneous gaseous reactions; the galvanic cell; electrode potentials; concentration cells and activities; electrolysis. The book is concise; it is pretty well written; and it can be recommended to students.

There are some things which should be changed in the next edition. Kirchhoff's name is misspelled throughout and Julius Thomsen suffers. Arragonite is probably a typographical error. In this country we should mean something different from what Mr. Butler does by the statement, p. 88, that "in general, an increase of pressure favours the state with the smallest volume." No student will see how one measures an electromotive force rather than a potential drop with a potentiometer, p. 109. This should be made clear or should be omitted. It is probable that the student will also be bothered a good deal by the thermionic work function, p. 124. Calomel should be written Hg_2Cl_2, p. 133, and the German spelling of cation is unfortunate, p. 143. Faraday was an Englishman.

On p. 79 is an illustration of how difficult it is to say just what one wishes to. The author has moved "the semipermeable piston up (gainst pressure P) until a quantity of solvent equal to that which gives one mol of the vapour has passed through it. If ΔV is the decrease in the volume of the solvent [solution?], the work done is $P\Delta V$."

. The author spoils it all by saying four lines lower that "it should be observed that ΔV is the volume of the solution containing that quantity of solvent which gives one mol of the vapour." If we had a solution containing benzene and toluene in the ratio of 78:92 in grams, the volume through which the piston would move to push out 78 grams of benzene would be less than one half the volume of the solution containing 78 grams of benzene, if we ignore the difference between the molecular volumes of benzene and toluene.

The activity coefficient of ten-molal hydrochloric acid is 10.55 and of sixteen-molal acid is 43.2, p. 161. As the author says, "the activities and activity coefficients are quantities which express the actual behaviour of substances in solution, without asserting that it is due to one effect or another. If the ions combine to form molecules to any extent, the effect on the behaviour is included in the activity," p. 167.

Wilder D. Bancroft

Polar Molecules. *By P. Debye. 23 × 15 cm; pp. 172. New York: Chemical Catalog Company, 1929. Price: $3.50.* In the preface the author says: "This book contains a survey of questions treated in connection with the conception of polar molecules as being systems having a distribution of electrical charges which can be characterized by a permanent electric moment. Since the appearance in 1912 of my first article many contributions on the experimental side of the problem have shown that absolute measurement of polarity based on this idea may successfully by used to determine the geometrical arrangement of the atoms in a molecule. On the theoretical side the introduction of the quantum theory in its most modern form has made it possible to develop in detail the connection existing between polarity and the phenomena of dispersion and absorption, especially in the infra-red. An interesting example of the inter-dependence of experiment and theory also resulting from the electrical definition of polarity is exhibited in the field of the electrical saturation phenomena, analogous to ferromagnetism," p. 3.

The chapters are entitled: fundamental electrostatic field relations; polarizability and molecular structure; measurements of polarity and its connection with chemical structure; the constitution of simple polar molecules; anomalous dispersion for radio frequencies; electrical saturation effects; dielectric phenomena and quantum theory; energy levels and wave mechanics; rotating molecules; dispersion and absorption of polar gases.

"The word polarity has been used in different ways to express molecular properties more or less connected with the actual arrangement, or the mobility of, the charges of which molecules are supposed to consist. All definitions have, in common, the feature that they are based on the fundamental picture according to which a molecule may be represented as a system of electric charges, and at the outset it is not at all necessary to decide as to whether those charges have to be taken as discrete units, or if the natural phenomena can be better represented by introducing a continuous distribution, more in agreement with the picture in modern quantum theory. The fundamental proposition being the electrical viewpoint, it is obvious that we may expect to advance our knowledge of molecules by studying more closely their behavior under the influence of a disturbing electric field. This field may be an external field, subject to our control, or may be the field created by other neighboring molecular systems. In the last case we will ultimately obtain an electrical theory of the equation of state; in the first case we are dealing with dielectric and optical properties. As the last named properties can be treated most simply, and still give us much insight into the molecular structure, we will in this treatise confine our attention chiefly to these dielectric and optical properties alone. A brief review of certain features of classical electrical theory will give the necessary foundation," p. 7.

When discussing the dielectric constants of ionic solutions, the author says, p. 112: "If, therefore, the water contains a number of ions, there will be a region around each ion which contains electrically saturated water. If we now superpose a small homogeneous external field in order to measure the dielectric constant of the electrolyte solution, the regions of the water surrounding the ions will be made more or less inactive due to their saturation. A very rough picture of this occurrence will be obtained if each ion with its surrounding water is replaced by a spherical cavity, the radius of which depends on the distance over which the saturation effect is appreciable," p. p. 112.

For small concentrations of an electrolyte the apparent dielectric constant decreases with increasing concentration, which is accounted for by the saturation, p. 114. "At higher concentrations it is found that the dielectric constant comes back to, and surpasses, the value for the pure solvent. The qualitative picture proposed to explain this concentration effect is that, at higher concentrations, an appreciable number of doublets may be formed by the coupling of positive and negative ions, and that these doublets will give an increase in the dielectric constant by their orientation. The question of a chemical interaction, resulting in a relatively permanent and definite coupling, being necessary, or of the coupling due to the interionic electric forces being sufficient, has not yet been treated," p. 144

"The whole subject of saturation in ionic solutions and connected phenomena has been treated in a highly hypothetical way. On the other hand the existing experiments are far from satisfactory. . . . The table shows clearly the big differences, even in magnitude, of the different experimenters. . . . The valency relation is satisfied most completely by the values of Sack, less completely by those of Skancke and Schreiner and of Walden and his collaborators, and not at all by those of Deubner. It is doubtful whether these differences can be explained by the differences in frequency. The fact is that no definite conclusions with regard to any theory can be drawn from the measurements in their present condition. Old methods will have to be improved and new methods introduced," p. 122.

The reviewer does not like the word "hydroiodic", p. 40; that seems to be a case of misguided purism. *Wilder D. Bancroft*

Reference Book of Inorganic Chemistry. *By Wendell M. Latimer and Joel H. Hildebrand. 22 × 15 cm; pp. viii + 643. New York: The Macmillan Company, 1929.* In the preface the authors say: "This book represents the fulfillment of a plan, long chreished, of providing a volume of descriptive chemistry to complete the series begun with "Principles of Chemistry" by Hildebrand, which adheres strictly to its title, and continued with the "Course in General Chemistry" by Bray and Latimer, which presents a laboratory course. The rather radical experiment in teaching general chemistry, begun in the University of California in 1912, has been somewhat hampered by the lack of a reference book on descriptive chemistry employing the language and the point of view adopted for our instructional scheme.

"This 'Reference Book of Inorganic Chemistry' has been written as a reference book rather than a text. The authors have sought to present essential chemical facts briefly, clearly, and in due relation to other facts and principles. The instructor using it will have to map out his own course, following whatever order of arrangement appeals to him. The numbering of paragraphs will make it possible for him to assign for study material selected from any desired portion of the book. We feel that many teachers will welcome the greater freedom thus afforded of developing their own pedagogical methods," p. v.

The chapters deal with: hydrogen; the inert gases; oxygen; alkali metals; alkaline earth metals; boron and aluminum; copper, silver, and gold; zinc, cadmium, and mercury; gallium, indium, and thallium; the halogens; nitrogen, phosphorous, arsenic, antimony, and bismuth; sulphur, selenium, and tellurium; carbon; silicon; the metals of Group IV; vanadium, columbium, and tantalum; chromium, molybdenum, tungsten, and uranium; manganese; iron, cobalt, and nickel; platinum and the palladium metals; scandium, yttrium and the rare earth metals; the radioactive metals.

This is far from being a pandemic chemistry; but it is a step in the right direction, and metals are taken up on p. 27. The book is distinctly an interesting one and well worth reading. The authors are a bit shaky on the difference between an adjective and an adverb, and the reviewer questions the statement, p. 280, that "excess of alkali hydroxide dissolves the precipitate [of chromic hydroxide] with the formation of chromites, but the hydroxide or hydrated oxide is precipitated upon boiling." Even for freshmen the reviewer would prefer a different wording in regard to ozone, p. 25. "The silent electrical discharge is the principal commercial method of forming ozone. This involves the action of electrons shot off from high-potential surfaces upon oxygen molecules."

One does not quite see why the crystal form of sodium nitrate should be sandwiched in between the method of making potassium nitrate and the fact that the alkali nitrates decompose when heated, p. 42.

Apart from a few infelicities, the authors are very much to be congratulated on this book. There is an immense amount of information packed into it, and it is presented in a clear and readable fashion. *Wilder D. Bancroft*

Le Soufflage du Verre. *By Henri Vigreux. 16 × 11 cm, pp. 276. Paris: Librairie Dunod, 1930. Price: 35 francs.* It is somewhat surprising that opportunities for learning glass blowing even by advanced students in physics and chemistry scarcely exist in England and reliance has to be placed upon self education and experience. Under these conditions any book which describes methods of glass blowing which really can be followed and acted upon would prove invaluable. There are but few text books on this subject and nearly all of these suffer from the defect that it is difficult to follow the directions. Dr. Vigreux's little book on glass blowing is a good book although it might be regarded from the English point of view as somewhat old fashioned. The directions given in the book are clear and intelligible. It contains an interesting history of early operations in glass, continues with practical methods for making first simple and then more complex apparatus and terminates somewhat surprisingly with cements, X-ray bulbs and artificial eyes. This book is already in its third edition and is to be warmly commended both to physicists and to chemists.

Eric K. Rideal

Optical Rotatory Power. *A General Discussion held by the Faraday Society. 25 × 16 cm; pp. ii + 197. London: Gurney and Jackson, 1930. Price: 10 shillings, 6 pence.* This volume is a separate issue of that part of the Transactions of the Faraday Society which contains the papers read at the general discussion held in London during last April and the comments that arose from the papers. The papers are classified on four groups, the physical basis of optical rotation, apparatus and methods, the rotatory power of solutions and finally the chemical aspects of rotatory power. In all there are twenty one papers together with an introduction and a concluding summary by Professor Lowry.

Reading through this volume gives one a very good impression of the present position of many of the diverse problems that await solution in this subject. The majority of the papers are summaries of investigations already published and, as such, will be of the greatest value. To the reviewer two of the most interesting are those of Kuhn and of Wolf. The former is a simplified exposition of Kuhn's theory of the physical basis of rotatory power which appeared in the *Zeitschrift für physikalische Chemie* last year; it is presented in an extremely able way and can be followed by those who do not possess an extensive mathematical equipment. The latter, that of Wolf, deals with the question of free rotation in saturated carbon compounds, and indicates a new method of investigating the extent of the freedom of rotation. As Wolf points out, classical stereochemistry was based on three postulates, of which two, constancy of atomic distances and constancy of valency angles, have been justified as first approximations by all recent methods of physical investigation. The third postulate, free rotation, however, has had to be abandoned in a few cases by even the most classical of stereochemists, so that this preliminary account of a physical investigation into the extent of free rotation is of the greatest interest. *T. W. J. Taylor*

Biological Applications of Absorption Spectrophotometry. *15 × 24 cm; pp. 12. London: Adam Hilger Ltd., 1930. Issued gratis.* The study of absorption spectra has in recent years occupied an important place in biochemical investigation, particularly with regard to vitamin A and vitamin D. Very interesting results have also been obtained with proteins, blood sera, biological pigments and the respiratory ferments. There are probably few fields of research in which hasty deductions and inadequate technique present greater dangers, and this publication is useful both in calling attention to the possibilities of absorption spectrophotometry and to the need for accuracy in gathering data and care in interpretation.

R. A. Morton

Erratum

Owing to an oversight on the part of the editor the legends were omitted from the cuts in the article by Levene and Rothen (34, 2567).

Fig. 1. The concentration of mandelic acid is 0.05N throughout, except in the case of $Ca(OH)_2$ where the concentrations are indicated in brackets on the curve.

Fig. 2. The concentration of sodium mandelate is constant and equal to 0.05N.

Fig. 3. The concentration is 0.05N in mandelic acid and in HCl.

THE STATISTICAL TREATMENT OF REACTION-VELOCITY DATA. I.

A Critical Review of Current Methods of Computation*

BY LOWELL J. REED AND EMERY J. THERIAULT

Introduction

In the study of reaction-velocity, although analyses and manipulations of unusual difficulty are frequently carried through, and a high order of mathematical skill is demanded, it is nevertheless true that, almost without exception, no attempt is made to estimate the degree of confidence which may be placed on the final results. In the absence of appropriate precision values it appears doubtful whether, in most cases, a decision can ever be reached concerning the validity of the proposed theories which prompt these laborious investigations..

In illustration of the point in question, let it be assumed that the critical increment for a given reaction is 50,000 ± 3,000. Such a deviation does not appear improbable in certain published results. Now, given the value of K_∞ from theoretical or other considerations, let the validity of a particular theory be tested by comparing a value of K_T calculated by the formula

$$K_T = K_\infty e^{\frac{-50{,}000 \pm 3{,}000}{RT}} = K_\infty e^{\frac{-50{,}000}{RT}} . e^{\frac{\pm 3{,}000}{RT}}$$

with an observed value of the velocity constant at the same temperature. When the temperature on the absolute scale is 328°, the numerical value of the term $e^{\frac{\pm 3{,}000}{RT}}$ is $10^{\pm 2.0}$, that is, the calculated value might be multiplied or divided by 100 without violence to the data. With this degree of latitude in the adjustment of the calculated value of K_T, the proof or disproof of proposed mechanisms of molecular behavior is obviously impossible.

In other directions a disregard of accepted statistical procedures has led to conclusions which must be accepted with caution. Thus the unimolecularity of the inversion phenomenon, for a long time the classical illustration of a "unimolecular" process, has been questioned on grounds of systematic divergencies in the velocity constants computed by the usual methods (cf. Pennycuick, 1926). Explanations based on the increasing activity of the sucrose or of the hydrogen-ion have been offered to account for increasing values of K, but no satisfactory theory appears to have been advanced to cover cases in which the trend in the K values is decidedly downward. In all of these studies, no account appears to be taken of the fact that, especially in work of the highest precision, a trend in the K values must inevitably be obtained when the usual methods of computation are employed.

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* From the Department of Biostatistics of the School of Hygiene and Public Health of the Johns Hopkins University, Paper No. 144, and the Stream Pollution Investigation Laboratory, United States Public Health Service.

In the main the statistical discussion which follows will be limited to a consideration of unimolecular reaction-velocity data. In the present paper it will be shown that the various methods in vogue for the calculation of velocity constants will by no means give equivalent results.

In a separate paper a detailed presentation will be given of a statistical procedure developed by us and already applied to the derivation of velocity constants in biochemical oxygenations (Theriault, 1927). The procedure in question will be expanded to cover cases where constant errors must be eliminated from the observations and appropriate methods for the derivation of precision values will also be given.

1. Nomenclature

For a unimolecular process, the differential equation representing the rate of reaction is

$$\frac{dY'}{dt'} = K(L'-Y') \tag{1}$$

or,

$$\frac{dZ'}{dt'} = -KZ' \tag{1a}$$

depending on whether attention is focused on the amount of material, Y', which has decomposed or on the amount of material, $Z' = L'-Y'$, which remains undecomposed at the time t'. The integration of these expressions between the concentration limits $(Y' = L'-Z')$ and $(Y_0' = L'-Z_0')$ and the corresponding time limits t' and t_0' gives

$$K = \frac{1}{t'-t_0'}\, ln\, \frac{L'-Y_0'}{L'-Y'} \tag{2}$$

or,

$$K = \frac{1}{t'-t_0'}\, ln\, \frac{Z_0'}{Z'} \tag{2a}$$

In equations (2) and (2a) the following significance attaches to the various symbols:

Y' = Amount of material decomposed (transformed, inverted, diffused, etc.) at the time t'.

Y_0' = Amount of material decomposed at the time, t_0'.

$Y'-Y_0'$ = Amount of material decomposed during the time interval $(t'-t_0')$.

L' = Amount of undecomposed material present when t' = zero; the limiting value of Y'.

$L'-Y_0' = Z_0'$ = Amount of undecomposed material present when $t' = t_0'$.

$L'-Y' = Z'$ = Amount of undecomposed material present at the time t'.

t' = Time which has elapsed since the start of the reaction.

t_0' = Time at which the observations were begun measured in terms of time elapsed since the start of the reaction.

For the purpose of placing equations (2) and (2a) in a more convenient form, it may be assumed in any given experiment that the observed quantities were

$$t = t' - t_0'$$
$$Y = Y' - Y_0'$$

and,

$$L = L' - Y_0' = Z_0' \tag{3}$$

Substituting in (2) and (2a)

$$K = \frac{1}{t} \ln \frac{L}{L-Y} \tag{4}$$

or,

$$K = \frac{1}{t} \ln \frac{L}{Z} \tag{4a}$$

Equations (4) and (4a) might also have been derived on the equivalent assumption that t_0' and Y_0' in equations (2) and (2a) were equal to zero. For the purposes of the present discussion it will be convenient, however, to assign to L, Y and Z the significance denoted by (3).

In addition to equations (4) and (4a), use will also be made of the expressions

$$Y = L\,(1-e^{-Kt}) \tag{5}$$

and,

$$Z = L\,e^{-Kt} \tag{5a}$$

obtained by solving for Y and Z in equations (4) and (4a).

2. The Usual Methods of Computation

Given a series of timed observations, $Y_1, Y_2, \ldots, Y_n$, of a supposedly unimolecular process, together with the corresponding times $t_1, t_2, \ldots, t_n$ and the experimentally determined value of L, the usual procedure in deriving the average value, $\overline{K}$, of K is, first of all, to calculate a series of K values, such as

$$\begin{aligned} K_1 &= \frac{1}{t_1} \ln \frac{L}{L-Y_1} \\ K_2 &= \frac{1}{t_2} \ln \frac{L}{L-Y_2} \\ &\ldots\ldots\ldots\ldots, \\ K_n &= \frac{1}{t_n} \ln \frac{L}{L-Y_n} \end{aligned} \tag{6}$$

If the series of K values obtained does not manifest an ascending or descending tendency, $\overline{K}$ is then found by taking the simple arithmetical average of $K_1, K_2, \ldots, K_n$.

An objection frequently raised against this procedure is that in deriving the values K_1, K_2, etc., the observation L is used 2n-times as frequently as the equally reliable observations $Y_1, Y_2, Y_3, \ldots, Y_n$. It may also be objected that the values of K in (6) are by no means possessed of an equal degree of reliability. Thus, during the early stages of the reaction, when the value of Y is small, the ratio $L/(L-Y)$ is nearly unity. Conversely, in the later stages of the reaction, the value of Y approaches to that of L and the ratio in question approaches infinity. In either case the logarithm of the ratio will be disproportionately affected by otherwise unimportant errors in the estimation of either L or Y. The conclusion appears warranted that in averaging the values of K derived by means of equations (6), some system of weighting should be employed.

It is of more consequence perhaps that even when Y is determined with great accuracy, a series of ascending or descending values of K must inevitably be obtained when equations (6) are used, unless L is entirely free from error. As L, in general, will always be affected by some experimental error, the above statement implies that when the method of computation under discussion is employed no chemical reaction can appear unimolecular throughout its course, provided that Y has been determined with sufficient precision. Thus, let it be assumed that Y has been determined with a high degree of precision so that the trend in the K values deduced under (6) is not masked by relatively large errors of observation. Let it be assumed that, if possible, L has also been determined with an equal degree of precision so that the true value, L′, of L differs from L by the small quantity s. In order to obtain the correct values of K_1, K_2, etc., use should therefore be made of the corrected expression

$$K = \frac{1}{t}\, ln \frac{L'}{L'-Y}$$

If, instead of this equation, use is made of the uncorrected expression,

$$K = \frac{1}{t}\, ln \frac{(L'+s)}{(L'+s)-Y} = \frac{1}{t}\, ln \frac{L}{L-Y}$$

the correct value of the fraction

$$\frac{L'+s}{(L'+s)-Y} = \frac{L}{L-Y}$$

will only be obtained when Y is zero. With increasing values of Y (and t) the numerator of the fraction will remain constant while the denominator decreases. The numerical value of the fraction will therefore increase disproportionately with time if s is negative and it will decrease too rapidly if s is positive. The logarithm of the fraction will show a corresponding increase or decrease. As the result of a constant error in L, an ascending or descending series of K values will therefore be obtained depending on whether the value of L is smaller or greater than its true value. From similar considerations it may readily be shown that a trend in the K values must result when the times t_1, t_2, t_3, etc., or the observations Y_1, Y_2, Y_3, are affected by constant errors superimposed on the usual plus or minus errors of observations.

An excellent example of the difficulty in question is afforded by the work of Pennycuick (1926). Using methods of utmost refinement, Pennycuick attempts to show that the inversion of sugar cannot be represented accurately by a formula of the unimolecular type, the basis for this conclusion being the presence of a decided trend in the K values computed by three different formulae. In explanation of this trend it is stated: "The decrease in water content and the increase in hydrogen-ion activity during inversion, are sufficient to explain the steady increase of the coefficients."

Scatchard (1926), accepting Pennycuick's findings in regard to a systematic divergence in the K values, points out that equation (1a) defining a unimolecular process does not apply to the values in question as the expression cannot be integrated unless K is given in terms of t. By a graphical method, Scatchard then deduces the following empirical relation between K and t

$$K = K_1 \, (1 - 0.03 \, e^{-0.01})$$

and by substitution in equation (1a) he derives the modified formula

$$\log \frac{Z_1}{Z_2} = K_1(t_2 - t_1) \left[1 - \frac{3}{t_2 - t_1} \left(e^{-0.01t_1} - e^{-0.01t_2} \right) \right]$$

When certain empirical allowances are made for constant time errors, the individual measurements are said to conform to the above formula with a mean deviation of 0.2 to 0.5 per cent, "so the agreement with the theory is as good as could be expected." Scatchard concludes: "The evidence for the increase in the hydrogen-ion activity appears sound, but these results indicate that there must be some compensating tendency to diminish the rate." The trend in the K values is ascribed to inefficient mixing. "Five hours does not appear too long for this process."

It will be shown in a subsequent section that, when appropriate methods of computation are used, the data of Pennycuick conform with great fidelity to the classical unimolecular expression.

In the light of the preceding discussion it would appear that, in work of the highest precision, the usual test for unimolecularity, namely the possibility of deriving a series of K values which do not manifest a trend, must be discarded. In less precise work, definite conclusions as to the unimolecularity of a process cannot, in general, be drawn. In such work a trend in the K values will nevertheless exist although it may be masked by counterbalancing positive or negative errors in the estimation of Y. In the presence of a trend the procedure of averaging a series of K values is open to serious objections, as the most reliable value of K may correspond not to the average of all the K values but rather to the first or last values in the series, depending on the sign of the constant error. In this sense the procedure of rejecting either the initial or the terminal results in a series of K values is obviously unsound (cf. Wobbe and Noyes, 1926).

As an alternative method of deriving the average value of K, use is also made of the "chain" or "short-time interval" formulae:

$$
\begin{aligned}
K_1 &= \frac{1}{t_2-t_1} \ln \frac{L-Y_1}{L-Y_2} \\
K_2 &= \frac{1}{t_3-t_2} \ln \frac{L-Y_2}{L-Y_3} \\
K_{n-1} &= \frac{1}{t_n-t_{n-1}} \ln \frac{L-Y_{n-1}}{L-Y_n}
\end{aligned}
\tag{7}
$$

If the logarithms, $\ln(L-Y_1)$, $\ln(L-Y_2)$, etc., in (7) are replaced by the symbols, N_1, N_2, etc., the average value of K is,

$$\overline{K} = \frac{1}{n-1}\left(\frac{N_1-N_2}{t_2-t_1} + \frac{N_2-N_3}{t_3-t_2} \cdots \frac{N_{n-1}-N_n}{t_n-t_{n-1}}\right) \tag{8}$$

In deriving the set of equations represented by (7) it is sometimes assumed (cf. Pennycuick, 1926, p. 11) that the individual values of K have been found by the subtraction of two expressions such as

$$K_{n-1} = \frac{1}{t_{n-1}} \ln \frac{L}{L-Y_{n-1}}$$

and,

$$K_n = \frac{1}{t_n} \ln \frac{L}{L-Y_n}$$

with the result

$$K_n t_n - K_{n-1} t_{n-1} = \ln \frac{L-Y_{n-1}}{L-Y_n} \tag{9}$$

If it be now assumed that $K_n = K_{n-1}$, it follows that

$$K = \frac{1}{t_n-t_{n-1}} \ln \frac{L-Y_{n-1}}{L-Y_n} \tag{10}$$

As the value of L is fixed, the transition from (9) to (10) is evidently forced. More logically, the set of equations given under (7) may be regarded as the result of substitution in (2); that is, the terms t_0' and Y_0' are successively assigned the values

$$t_1, Y_1 \; ; \; t_2, Y_2 \; ; \text{etc.}$$

As to the merits of equations (7), it is to be noted that, as in the corresponding equations (6), the observation L is repeated n-times as frequently as the observations Y_1, Y_2, etc. Another objection relates to a cancellation effect which will briefly be discussed.

Let it be assumed that the observations have all been equally spaced in respect to time, so that

$$(t_2-t_1) = (t_3-t_2) \ldots\ldots = (t_n-t_{n-1}) = \Delta t$$

Under this condition, equation (8) reduces to the simple form

$$\overline{K} = \frac{N_1-N_n}{(n-1)\Delta t} = \frac{N_1-N_n}{t_n-t_1} = \frac{1}{t_n-t_1} \, ln \, \frac{L-Y_1}{L-Y_n}$$

that is, only the first and last observations are considered in deriving the average value of K (cf. Wagner, 1923, p. 132).

In this case, it is obvious that errors of any order of magnitude in the estimation of the intermediate values, Y_2, Y_3, ..., Y_{n-1}, would be without influence in the final result. The data of Daniels and Johnston (1921, p. 64; their experiment No. 25) afford an example of this method of calculation. On the basis of 6 observations equally spaced at one-minute intervals, they compute 5 values of K by means of equations (7). They then deduce the average value of K by the formula

$$\overline{K} = \frac{K_1 + K_2 + K_3 + K_4 + K_5}{5}$$

$$= \frac{337 + 288 + 329 + 434 + 337}{5 \times 10^3} = 345 \times 10^{-3}$$

Using equation (2) and neglecting the intermediate observations, the result is the same, namely

$$\overline{K} = \frac{2.303}{7-2} \log \frac{32.6 - 18.6}{32.6 - 30.1} = 345 \times 10^{-3}$$

The cancellation effect in question is also apparent in all of the other data presented by Daniels and Johnston (1921) even though the time intervals may vary in a given experiment. Thus, in their experiment No. 23, the first nine observations are separated by one-minute intervals while the remaining three observations are spaced 2 minutes apart. Equation (8) accordingly assumes the form

$$\overline{K} = \frac{2.303}{11}\left(\log \frac{L-Y_1}{L-Y_8} + \frac{1}{2} \log \frac{L-Y_8}{L-Y_{11}}\right)$$

$$= \frac{2.303}{11}\left(\log \frac{319.5 - 128.2}{319.5 - 299.4} + \frac{1}{2} \log \frac{319.5 - 299.4}{319.5 - 316.5}\right)$$

$$= 291.3 \times 10^{-3}$$

a result which accords exactly with the true average* of the eleven K values given by Daniels and Johnston, although only three observations were used in the computation. It is obvious that, in general, a "chain" formula should not be used in determining the average value of K. Neither should such a formula be employed as a means of detecting a trend in the value of K, as the trend, although present, will be masked by the occurrence of alternate high and low values of K whenever a relatively large error occurs in the observations.

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* The average value given by Daniels and Johnston ($K = 290.0 \times 10^{-3}$) is apparently in error. The value 291.3×10^{-3} accords with the true average of their figures. The difference may arise from minor typographical errors or else it may be due to the use of some system of weighting.

In passing, it may be noted that "chain" formulae are generally used when the times, t_1, t_2, etc., are known to be affected by an appreciable constant error. A constant error in the determination of t_1, t_2, etc., will evidently cancel out when expressions such as (t_2-t_1), etc., are used. However, even when the observations are not equally spaced, this procedure gives undue weight to the initial and final observations. It is also to be noted that, at best, this method of computation neglects another important source of constant error, namely the constant error in L.

3. Miscellaneous Methods of Computation

Guggenheimer (1926) considers that the procedures thus far discussed are justifiable only when the value of L has been determined with appreciably greater precision than the other observations, Y_1, Y_2, etc. However, "Not infrequently it is inconvenient or even impossible to observe the end-point (L) directly at all; in such cases it is usual to obtain a value for it by extrapolation. If this is done by any straightforward method the value of L obtained will, at best, be no more accurate than any of the directly observed values of Y. The best value of K will not then be obtained by any of the usual methods which give great weight to L." To obviate the difficulty in respect to the undue weighting of L, Guggenheimer proposes that n readings Y_1, Y_2, Y_3, etc., be made at the times t_1, t_2, ..., t (without any restrictions as to the intervals) and that n more readings Y_1', Y_2', etc., be made at the times (t_1+r), (t_2+r), ... (t_n+r) each a constant time r after one of the previous set. "Provided that r is several times as great as the time of half-completion of the reaction, the accuracy will be of the same order as in taking n ordinary readings and further taking n readings of the end-point spread over an interval of time equal to that spent on the ordinary readings; in fact, it is equivalent to obtaining a very accurate end-point and using it in the usual manner."

Sheppard (1926; cf. Sheppard and Mees, 1907) has shown that if two observations only are to be made, it may be advantageous to select them in such a manner that $t_2 = 2t_1$. Then, using equation (4)

$$K = K_1 = \frac{1}{t_1} \ln \frac{L}{L-Y_1} \tag{11}$$

$$K = K_2 = \frac{1}{2t_1} \ln \frac{L}{L-Y_2} \tag{12}$$

The assumption $K = K_1 = K_2$ is justifiable if only two observations are at hand, provided that the value of L is not fixed. On dividing (11) by (12) and solving for L, the result is

$$L = \frac{Y_1^2}{2Y_1 - Y_2} \tag{13}$$

Equation (13) gives L in terms of the two observations Y_1 and Y_2. By substitution in (11) or (12), the value of K may therefore be determined. This method of computation has also been discussed by Smith (1926) who states that the procedure can be extended to bimolecular reactions. This extension, however, is not formulated by Smith.

Guggenheimer (1926) considers that it would be a more natural procedure, instead of eliminating K, to eliminate L. Thus, using equation (5), let two observational equations be

$$Y_2 = L\left(1 - e^{-2Kt_1}\right) \tag{14}$$

and,

$$Y_1 = L\left(1 - e^{-Kt_1}\right) \tag{15}$$

By division,

$$\frac{Y_2}{Y_1} = \frac{1 - e^{-2Kt_1}}{1 - e^{-Kt_1}} = 1 + e^{-Kt_1}$$

From which,

$$K = \frac{1}{t_1} \ln \frac{Y_1}{Y_2 - Y_1} \tag{16}$$

Equation (16) gives the value of K in terms of two observations Y_1 and Y_2 and without reference to L.

The procedures just described are evidently designed for use in orientation experiments where approximate values of K or L are desirable or in cases where the direct estimation of L is inconvenient or impossible. The results obtained will evidently possess a minimum of reliability as the computation, without resort to weighting, must be restricted to the minimum number of possible observations, namely two, corresponding to the two constants L and K in equations (4) or (5). In special cases approximate values of K and L may even more readily be obtained by the use of nomographical charts (Buchanan, 1926) or by mechanical means (Latshaw, 1925).

Schmid (1926) has proposed a method of calculating K which possesses certain points of interest. Starting with the set of equations

$$\begin{aligned} K_1 &= \frac{N_1 - N_2}{t_2 - t_1} \\ K_3 &= \frac{N_3 - N_4}{t_4 - t_3} \\ K_5 &= \frac{N_5 - N_6}{t_6 - t_5} \end{aligned} \tag{17}$$

where $N_1 = \ln(L - Y_1)$; $N_2 = \ln(L - Y_2)$, etc. Schmid apparently assumes that the relative weights of the individual values K_1, K_3, etc., are $(t_2 - t_1)$, $(t_4 - t_3)$, etc. The weighted average of K then becomes

$$\bar{K} = \frac{(t_2-t_1)(K_1) + (t_4-t_3)(K_3) + (t_6-t_5)(K_5)}{(t_2-t_1) + (t_4-t_3) + (t_6-t_5)} \tag{18}$$

On substituting from (17) in (18), there results the simple formula

$$\bar{K} = \frac{N_1-N_2 + N_3-N_4 + N_5-N_6}{-t_1 + t_2 - t_3 + t_4 - t_5 + t_6} \tag{19}$$

It is claimed by Schmid that his formula involves a minimum of arithmetical work; also that the precision with which K is determined is equal to that attainable by the method of least-squares. The system of weighting implied in Schmid's formula is obviously arbitrary.

Rice, Fryling and Wesolowski (1924), in extension of the work of Rice and Kirkpatrick (1923), have proposed a system for weighting the values of K obtained by equations (6) when the observed quantity is $Z = L-Y$. Assuming that t is relatively free from error, they first derive the partial derivatives of K with respect to Z and L in the expression

$$Z = Le^{-Kt}$$

and so obtain

$$\frac{\delta K}{\delta L} = \frac{1}{tL}$$

and,

$$\frac{\delta K}{\delta Z} = \frac{1}{tZ}$$

From which the partial fractional errors in K become

$$\left(\frac{\delta K}{K}\right)_L = \frac{\delta L}{KtL} = \frac{\delta L}{L} \div \ln \frac{L}{Z} \tag{20}$$

and,

$$\left(\frac{\delta K}{K}\right)_Z = \frac{\delta Z}{KtZ} = \frac{\delta Z}{Z} \div \ln \frac{L}{Z} \tag{21}$$

On the tacit assumption that the absolute error in Z will be of the same order of magnitude as that in L, they then express $\delta Z/Z$ in terms of $\delta L/L$. Thus,

$$\frac{\delta Z}{Z} = \frac{\delta L}{Z} = \frac{\delta L}{L} \cdot \frac{L}{Z}$$

Substituting in (21),

$$\left(\frac{\delta K}{K}\right)_Z = \frac{\delta L}{L}\left(\frac{L}{Z}\right) \div \ln \frac{L}{Z} \tag{22}$$

The total (fractional) error in K is then assumed to be given by the square root of the sum of the squares of the partial fractional errors; so that, using (20) and (22),

$$\frac{\Delta K}{K} = \sqrt{\left(\frac{\delta K}{K}\right)_L^2 + \left(\frac{\delta K}{K}\right)_Z^2} = \frac{\delta L}{L}\,\frac{\sqrt{1 + \left(\frac{L}{Z}\right)^2}}{\ln\frac{L}{Z}} \tag{23}$$

$$= \frac{\delta L}{L} \cdot F(L,Z) = \frac{\delta Z}{L} \cdot F'(L,Z)$$

Somewhat arbitrarily, the quantity F(L,Z) is then defined as the weight of K. On plotting this function against the fraction, $1 - Z/L$, of material which has reacted, the conclusion is reached that the maximum relative weight of K is reached when a unimolecular reaction is 66 per cent completed.

In criticism of the system of weighting proposed by Rice, Fryling and Wesolòwski, it may be objected that, at best, such procedures are applicable only to series of K values which do not show a trend. As already shown, this condition will rarely be satisfied when an accurate series of observations is made. Otherwise stated, such treatments make no allowance for the presence of constant errors.

In another direction, the procedure proposed by Rice, Fryling and Wesolowski is open to the objection that, unless each value of L in equations (6) represents an independent observation (cf. Guggenheimer, 1926), the error δL will be a constant throughout a series of calculations. On the other hand, δY may be regarded as an error which is equally likely to be positive or negative. It is only when L is a quantity affected by plus or minus errors that the step represented by equation (23) would be justifiable.

If L is regarded as a true constant, the differentiation of the expression

$$Y = L(1 - e^{-Kt})$$

gives,

$$\Delta Y = L\,t\,e^{-Kt}\,.\,\delta K$$

From which

$$\Delta K = \frac{\delta Y}{L(te^{-Kt})}$$

It follows that, for minute variations in K, the error ΔK will be a minimum when the function $t\,e^{-Kt}$ is a maximum. Such a maximum will occur when

$$\frac{d(t\,e^{-Kt})}{dt} = e^{-Kt} - K\,t\,e^{-Kt} = 0$$

From which, when ΔK is a minimum,

$$K = 1/t$$

Using equation (5), it may readily be shown that, under the assumed conditions, the fraction of material used up will be

$$Y/L = 1 - e^{-1} = 1 - \frac{1}{2.71} = 0.632$$

If the assumption regarding the constancy of L is ever justified, it would appear that a velocity constant will be determined with a maximum of precision when the period of observation is so selected that the reaction has proceeded to the extent of 63.2 per cent. On the same basis the weight of a given value of K might be expressed in terms of the function $t\,e^{-Kt}$. Such a procedure would evidently be inapplicable to ascending or descending series of K values.

If L and Z are both regarded as variables the following treatment should apply. For convenience, the equation

$$Z = L\,e^{-Kt}$$

will first be placed in the equivalent form

$$Kt = ln\,\frac{L}{Z} = ln\,L - ln\,Z$$

From which,

$$t\Delta K = \frac{\delta L}{L} - \frac{\delta Z}{Z}$$

Now, if it is assumed that the error in L is of the same order of magnitude as that in Z, we may write

$$Kt.\,\frac{\Delta K}{K} = \frac{\delta L}{L} - \frac{L}{L}\cdot\frac{\delta L}{Z} = \frac{\delta L}{L}\,(1 - \frac{L}{Z})$$

Substituting the value of Kt and transposing, it follows that

$$\frac{\Delta K}{K} = \frac{\delta L}{L}\cdot\frac{(1 - L/Z)}{ln\,L/Z} \qquad (23a)$$

Equation (23a) may be compared with equation (23). The difference between these two functions arises from the fact that there is correlation in errors between the two terms $(\delta K/K)_Z$ and $(\delta K/K)_L$ whereas the formulation of equation (23), based on the theorem relating to the square root of the sum of the squares of partial fractional errors, presupposes the absence of such correlation. The difficulty is avoided by deriving $\Delta K/K$ directly as shown above.

If L and K are regarded as quantities affected by errors of observation and if t is free from error, the partial differentiation of equations (4) and (4a) gives, respectively,

$$\Delta Y = (1 - e^{-Kt})\,.\,\delta L + L\,t\,e^{-Kt}\,.\,\delta K$$

and,

$$\Delta Z = e^{-Kt}\,.\,\delta L - L\,t\,e^{-Kt}\,.\,\delta K \qquad (24)$$

By substitution in these equations of the approximate values of K and L, it would be possible to estimate the effect on Y or Z of arbitrarily selected values of δL and δK and so obtain some idea of the precision with which Y or Z must be determined in order to secure a given degree of precision in K or L. Conversely, and with particular reference to the treatment proposed by Rice, Fryling and Wesolowski, if ΔZ if regarded, say, as the difference between an observed quantity, Z, and a calculated quantity Z' obtained by substituting known values of K and L in (4a), then the value of δK (and δL) could be found by elimination from two equations such as (24). However, if more than two equations are available, the solution becomes indeterminate and resort must be made to the method of least-squares.

4. Attempted Applications of Least Squares

The shortcomings of the procedures thus far discussed have prompted at least three writers to attempt a solution of the problem by the application of the least-squares criterion.

Moesveld (1923) has discussed the least-squares treatment of data pertaining to reactions of the second or higher orders. For such reactions,

$$\frac{dY}{dt} = K(A-Y)^a(B-Y)^b(C-Y)^c(D-Y)^d \text{ etc.}$$

For the special case, $A = B = C \ldots\ldots = L$ and $a = b = c \ldots\ldots = n$

$$\frac{dY}{dt} = K(L-Y)^n$$

The integration of this expression gives

$$K = \frac{1}{(n-1)t}\left(\frac{1}{(L-Y)^{n-1}} - \frac{1}{L^{n-1}}\right)$$

For the supposedly fourth-order reaction which Moesveld uses as an example,

$$K = \frac{1}{3t}\left(\frac{1}{(L-Y)^3} - \frac{1}{L^3}\right).$$

From which,

$$\frac{1}{(L-Y)^3} = 3Kt + \frac{1}{L^3}$$

or, $$W^3 = K't + W_0^3 \tag{25}$$

where, $$W^3 = \frac{1}{(L-Y)^3};\ W_0^3 = \frac{1}{L^3};\ K' = 3K$$

Moesveld then places equation (25) in the form

$$Y = af_1 + bf_2 \tag{26}$$

where, $Y = W^3;\ a = 3K;\ f_1 = t;\ b = W_0^3;\ f_2 = 1$

As will be shown elsewhere, the least-squares solution of a series of equations such as (26) gives the following values for the constants a and b

$$a = \frac{n\,.\,\Sigma f_1Y - \Sigma f_1\,.\,\Sigma Y}{n\Sigma f_1^2 - (\Sigma f_1)^2} \tag{27}$$

$$b = \frac{\Sigma f_1^2\,.\,\Sigma Y - \Sigma f_1\,.\,\Sigma f_1Y}{n\Sigma f_1^2 - (\Sigma f_1)^2} \tag{28}$$

For the purpose of simplifying the computations, Moesveld recommends that the periods of observation be selected in such a manner that $\Sigma f_1 = \Sigma t = 0$. This is accomplished by making an uneven number of observations and by spacing the observations symmetrically in respect to the middle observation. If the center of coordinates is then referred to the middle observation, the term $\Sigma f_1 = \Sigma t$ will be of the form

$$-\frac{(n-1)}{2} \;\ldots\; -6 \; -5 \; -4 \ldots\ldots 0 \ldots\ldots +4 \; +5 \; +6 \ldots\ldots \frac{n-1}{2} = 0$$

Whenever this arrangement is possible,

$$a = \frac{\Sigma f_1 Y}{\Sigma f_1^2} = 3K \qquad (29)$$

$$b = \frac{\Sigma Y}{n} = \frac{1}{L^3} \qquad (30)$$

As claimed by Moesveld, the computation of K and L using equations (29) and (30) is less laborious than the usual computation by means of equations (27) and (28). However, it must be noted that, in general, a precise arrangement of the periods of observation according to Moesveld's scheme could be only accomplished with very slow reactions. Moreover, the use of equation (25) as a basis of computation introduces the quantity

$$Y = W^3 = \frac{1}{(L-Y)^3}$$

although in Moesveld's experiments the quantity actually observed (resistance method) was $W = 1/(L-Y) = 1/Z$. No account is taken by Moesveld of the possible effect of this substitution on the least-squares treatment.

The difficulty in question appears to have been partly recognized by Wagner (1923), who proposed a system for weighting the observational equations. Considering the special case of the second-order reaction represented by the equation

$$1/(L-Y) = Kt + 1/L$$

or,

$$1/Z = Kt + J$$

Wagner assumes that the standard deviation, σ, of Z does not depend on the magnitude of Z. For the standard deviation of $1/Z$ he deduces σ/Z^2 and for the weight of any observational equation he writes $p = Z^4$. The weighted observational equations used by Wagner are accordingly of the type

$$Z_1^4\,(1/Z_1 - Kt_1 - J) = 0$$

or, in general,

$$p\,(1/Z - Kt - J) = 0$$

where p denotes the weights Z_1^4, Z_2^4, etc. His normal equations are

$$a\Sigma f_1^2 Z^4 + b\Sigma f_1 Z^4 - \Sigma f_1 Z^4 = 0$$

$$a\Sigma f_1Z^4 + b\Sigma Z^4 - \Sigma Z^3 = 0$$

where a = K and b = J = 1/L. From this he deduces

$$a = K = \frac{\Sigma Z^4 \,.\, \Sigma f_1Z^3 - \Sigma f_1Z^4 \,.\, \Sigma Z^3}{\Sigma Z^4 \,.\, \Sigma f_1^2Z^4 - (\Sigma f_1Z^4)^2}$$

$$J = 1/L = \frac{\Sigma f_1^2Z^4 \,.\, \Sigma Z^3 - \Sigma f_1Z^4 \,.\, \Sigma f_1Z^3}{\Sigma Z^4 \,.\, \Sigma f_1^2Z^4 - (\Sigma f_1Z^4)^2}$$

For the standard deviation ("mittleren Fehler;" mean error) of K, Wagner gives

$$\sigma_K = \sigma_y \,.\, \sqrt{\frac{\Sigma Z^4}{\Sigma Z^4 \,.\, \Sigma f_1^2Z^4 - (\Sigma f_1Z^4)^2}}$$

Wagner (p. 135) also considers the question of how a given number of observations should be arranged so as to obtain the most precise value of K. When 5 observations are to be made at two different concentrations, the concentrations Z_1 and Z_2 should be related in the sense that $Z_2 = 0.456\ Z_1$ and 4 of the 5 observations should be made at the concentration Z_2. It is stated that a fixed spacing of the observations is necessary only for the detection of systematic trends. The derivation of the factor, 0.456, is not given.

Before presenting any criticism of the statistical procedures proposed by Moesveld and by Wagner, it should first be recalled that in applying the Gaussian method of solution to a set of observational equations, it is generally necessary to place the equations in the linear form, $Y = af_1 + bf_2 + cf_3$, etc. It should also be borne in mind that the least-squares treatment is inapplicable to the solution of observational equations unless the observational and, accordingly, the residual errors are known to follow the normal curve of error. Thus, in the equation

$$Z = 1/(Kt + J)$$

used by Wagner, let it be assumed that the errors in the directly observed quantity Z are normally distributed. It follows that the residual errors, r_1, r_2, etc., represented by the expression

$$r = Z - 1/(Kt + J)$$

will also be normally distributed. This last equation, however, is not in the linear form and, if the distribution of the residual errors is not to be disturbed, it could only be placed in the linear form by the linearization of the term 1/(Kt+J). This difficulty is avoided by Wagner through the use of observational equations of the type

$$1/Z = Kt + 1/L$$

Now this expression (and the similar expression

$$1/Z^3 = 3Kt + 1/L^3$$

used by Moesveld) may be linearized by replacing 1/Z (or $1/Z^3$) by Y. For Wagner's equation, however, the expression for the residual errors becomes

$$r' = 1/Z - Kt + 1/L$$

and the condition imposed regarding the symmetrical distribution of the residual errors is obviously disturbed. Weighting of the observational equations does not satisfactorily correct the difficulty. For the bimolecular reaction in question, the problem could be simplified by making direct observations on the quantity $1/Z$. Moesveld has done this by using an electrical resistance method, but his further treatment is invalidated by the use of an equation in which the quantity presumably affected by the usual plus and minus errors is $1/Z^3$. For Moesveld's data the equation representing the residual errors should be

$$r'' = 1/Z - \sqrt[3]{3Kt + 1/L^3}$$

In this equation, the possibility of applying the Gaussian method of solution would depend on the linearization of the term under the radical sign.

For these and other reasons the statement by Moesveld that his treatment can be extended to unimolecular equations is to be accepted with caution. Thus, the equation

$$K = 1/t \ln L/(L-Y)$$

may be linearized by placing it in the form

$$\ln (L-Y) = \ln L - Kt$$

This expression is obviously of the type

$$Y' = a + bf_2$$

This transformation could be used when the quantity directly observed was $\ln (L-Y)$, provided that the errors in $\ln (L-Y)$ are symmetrically distributed. In general, it could not properly be used when the course of the reaction was followed by direct measurements of Y or $L-Y$.

Summary

1. The usual test for unimolecularity, namely, the possibility of deriving a consistent series of K values, should be discarded.
2. The least-squares procedures which have been described in the chemical literature are inapplicable to unimolecular data.
3. Proposed systems for the weighting of unimolecular constants are inapplicable in the presence of constant errors.
4. Appropriate methods for the derivation of weighted constants from observational equations of the unimolecular type will be described in a separate paper.

References

Buchanan, R. E., (1926): Nomogram for the determination of generation time and velocity coefficient for rates of growth or death. Iowa State College, J. Sci., **1**, (1), 63-65.

Daniels, F., and Johnston, E. H., (1921): The thermal decomposition of gaseous nitrogen pentoxide. A monomolecular reaction. J. Am. Chem. Soc., **43**, 53-71.

Guggenheimer, E. A., (1926): On the determination of the velocity constant of a unimolecular equation. Phil. Mag. (7) **2**, 538-43.

Latshaw, M., (1925): A simple tangimeter. J. Am. Chem. Soc., **47**, 793-4.

Moesveld, A. L. Th., (1923): Uber die Berechnung von Geschwindigkeitskonstanten. Z. physik. Chem., **103**, 481-5.

Pennycuick., S. W., (1926): The unimolecularity of the inversion process. J. Am. Chem. Soc., **48**, 6-19.

Rice, F. O., and Kirkpatrick, Jr., M., (1923): The measurement of reaction velocity and the temperature coefficient of reaction velocity. J. Am. Chem. Soc., **45**, 1402-5.

Rice, F. O., Fryling, C. F., and Wesolowski, W. A., (1924): The relation between the temperature coefficient and the mechanism of a chemical reaction. J. Am. Chem. Soc., **46**, 2410-13.

Scatchard, G., (1926): The unimolecularity of the inversion process. J. Am. Chem. Soc., **48**, 2259-63.

Schmid, G., (1926): Uber die Berechnung von Geschwindigkeitskonstanten. Z. physik. Chem., **119**, 8-18.

Sheppard, S. E., (1926): Some consideration of the reaction constant equation, and a simple method of determining the endpoint. Phil. Mag. (7) **2**, 448. Priority claim; cf. Smith (1926).

Sheppard, S. E., and Mees, C. E. K., (1927): "Investigation on the theory of photographic processes," p. 65; cit. Sheppard (1926).

Smith, R. C., (1926): Some considerations of the reaction-constant equation, and a simple method of determining the end-point. Phil. Mag. (7) **1**, 496-9.

Theriault, E. J., (1927): The oxygen demand of polluted waters. Public Health Bulletin No. 173, Appendix IV, pp. 174-185.

Wagner, C., (1925): Uber die Berechnung von Geschwindigkeitskonstanten. Z. physik. Chem., **115**, 130-6.

Wobbe, S. E., and Noyes Jr., W. A., (1926): Photochemical studies: IV. The thermal decomposition of anhydrous oxalic acid and its relation to the photochemical decomposition. J. Am. Chem. Soc., **48**, 2856-68; cf. Table III, p. 2864.

THE FICTIVE VOLUMES OF SODIUM SULPHATE IN AQUEOUS SOLUTIONS OF SULPHURIC ACID AND OF IODINE IN AN AQUEOUS SOLUTION OF POTASSIUM IODIDE

BY R. E. GIBSON

Introduction

The fictive volume v_2 of a solute in a solution of any concentration may be defined as the increase in volume produced by the introduction of one gram of the solute into an infinitely large volume of that particular solution. If V is the total volume of the solution and m_2 the mass of solute in that volume, v_2 is defined by the equation

$$v_2 = \left(\frac{\partial V}{\partial m_2}\right)_{p,t,m_1}$$

The partial molal volume is the fictive volume multiplied by the assumed molecular weight of the solute. If v_0 is the specific volume of the pure solute in the liquid state and if the solute and solvent form ideal solutions over the whole range of concentration, then $v_2 = v_0$. If, however, the solutions are not ideal, the expression $(v_0 - v_2)$ may be taken as a measure of the departure from ideality or of the specific interaction between solute and solvent.[1]

In particular, strong attractive forces between solvent and solute will result in $(v_0 - v_2)$ having a large positive value while repulsive forces between molecules of solvent and solute will lead to negative values for $(v_0 - v_2)$. If $(v_0 - v_2)$ is zero, we can say that the molecules of solute are no more or no less strongly attracted to molecules of solvent than they are to themselves.

In this paper I propose to examine the fictive volumes of two solutes in solutions in which chemical-compound formation, the result of intense interaction between solvent and solute, has been presumed to take place. In the first case sodium sulphate is the solute and the solvent consists of 5 and 10 per cent solutions of sulphuric acid. As the ratio of H_2SO_4 to water is kept constant throughout each series, the sulphuric acid solution may be taken as the solvent. It will be shown that in this system there are distinct peculiarities in the fictive volume-concentration curves which may be connected with the formation of $NaHSO_4$ in solution.

In the second case a concentrated solution of potassium iodide is used as solvent and iodine is the solute.

Experimental

Part 1. The first part of the experimental work consisted in determining accurately at 25° the specific volumes of two series of solutions, Series I, solutions of Na_2SO_4 in 4.818 per cent aqueous sulphuric acid, and Series II, solutions of Na_2SO_4 in 9.333 per cent aqueous sulphuric acid.

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[1] For discussion see J. H. Hildebrand: "Solubility," 62 ff. (1924).

The aqueous sulphuric acid was made from J. T. Baker's C.P. Analyzed H_2SO_4 and stored in five-litre Resistance Glass bottles provided with glass syphon, stopcock, and trap for excluding atmospheric moisture. In the preparations of the solutions of sodium sulphate, the anhydrous salt, obtained by recrystallization and subsequent dehydration of J. T. Baker's C.P. Analyzed sodium sulphate, was weighed by difference in a 100 cc stoppered flask and to it was added the requisite amount of sulphuric acid solution. The whole was then weighed, thoroughly mixed and kept at a temperature above 25° so that no air bubbles might form in the pycnometer.

The specific volumes were determined by a pycnometer method. The apparatus was that used and described in a previous paper[1] and the same technique was adhered to throughout. The pycnometer was recalibrated with pure water and its volume was found to be the same as before—55.0373 millilitres. The weight of the water content was 54.8762 grams as against an average of 54.8756 grams for the previous work.

The solutions of sulphuric acid were not analyzed, as their densities, combined with the tables of density as a function of concentration of Domke[2] gave an excellent method of determining the concentration of H_2SO_4. Before and after each series the specific volume of the sulphuric acid solution used was determined. The results agreed well, thereby giving the assurance that no change had taken place in the sulphuric acid during the work.

The experimental results are given in Tables I and II. The weighings are all corrected to vacuum, due regard being paid to the meteorological conditions at the time of the experiment. As I have now a fair confidence in the method, I duplicated the determination on only one Na_2SO_4 solution. The result was satisfactory, as a glance at the 6th and 7th rows in Table III will show.

TABLE I

Specific Volumes of Solutions of Na_2SO_4 in 5% H_2SO_4
Experimental Results at 25°

Weight of salt	Weight of solution	Concentration per cent (x_2)	Weight of soln. in pycnometer	Specific volume (v)
		0	56.6230	0.97198_1
		0	56.6233	0.97197_7
0.9975	102.3168	0.9749	57.0462	0.96477_1
2.0036	102.4381	1.9559	57.4779	0.95752_4
3.6054	100.0582	3.6033	58.2229	0.94527_8
5.0284	102.8749	4.8879	58.8212	0.93565_7
5.0073	102.4592	4.8871	58.8206	0.93566_7
11.2984	109.8719	10.2833	61.4846	0.89512_1
15.9422	104.2579	15.2911	64.1376	0.85810_8
20.9849	101.9319	20.5871	67.1031	0.82017_2
20.1725	87.2351	23.1243	68.5810	0.80250_4

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[1] R. E. Gibson: J. Phys. Chem., **31**, 496 (1927).

[2] Landolt-Börnstein: "Physikalisch-chemische Tabellen," 397 (1923).

TABLE II

Specific Volumes of Solutions of Na_2SO_4 in 10% H_2SO_4

Experimental Results at 25°

Weight of salt	Weight of solution	Concentration per cent (x_2)	Weight of soln. in pycnometer	Specific volume (v)
		0	58.3041	0.94395_7
		0	58.3040	0.94395_8
1.2018	103.2458	1.1640	58.8003	0.93598_9
2.0869	100.5386	2.0758	59.1955	0.92974_2
3.5075	104.5824	3.3538	59.7559	0.92102_2
5.5054	105.7186	5.2076	60.5889	0.90836_0
10.8726	109.2192	9.9548	62.8289	0.87597_4
15.8660	111.6128	14.2152	64.9817	0.84695_4
20.5285	113.3373	18.1127	67.0648	0.82064_6
26.0016	116.6655	22.2873	69.4085	0.79293_7
26.0549	104.2839	24.9846	70.9808	0.77537_2
30.0904	105.6213	28.4890	73.0915	0.75298_1

Part 2. In the second half of the experimental work measurements were made of the specific volumes of a series of solutions of iodine in a concentrated solution of potassium iodide, prepared by dissolving J. T. Baker's C.P. Analyzed KI, twice recrystallized, in air-free distilled water. The density of the solution was accurately determined as 1.52106, which according to the International Critical Tables[1] corresponds to a solution containing 48.72 per cent of KI. The solutions of iodine were prepared by successive dilution starting from Solution I, the most concentrated, which was prepared by dissolving a weighed amount of Merck's Reagent Iodine in the KI solution. The next solution was prepared by mixing weighed amounts of Solution I and the standard KI solution and so on for subsequent dilutions. Care was taken to preserve the solutions from contamination or evaporation at any stage in the investigation. Exactly the same apparatus was used but a special technique was required for introducing the concentrated iodine solutions into the pycnometer. The experimental results are recorded in Table VII. Unfortunately, there was not a sufficient amount of the standard potassium iodide solution left at the end of the series to admit of a check determination of its density.

Calculation of Results

For each series of sulphate solutions two simple equations were found adequate to express the results. These equations, which express the specific volume v as a function of the weight per cent of Na_2SO_4 in the solution, x_2, are as follows:

$$\left.\begin{array}{l} \text{Eqn.}(1)\ v=0.971980-0.00743x_2 \\ \text{Eqn.}(2)\ v=0.895127-0.007514(x_2-10.2833)+0.00002(x_2-10.2833)^2 \end{array}\right\}\ \text{Series I}$$

$$\left.\begin{array}{l} \text{Eqn.}(3)\ v=0.943957-0.006820x_2 \\ \text{Eqn.}(4)\ v=0.875664-0.006830(x_2-10)+0.000010(x_2-10)^2 \end{array}\right\}\ \text{Series II}$$

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[1] "International Critical Tables," 3, 88.

Equations (1) and (3) hold for the more dilute solutions from 1 to 15 per cent and the quadratic equations (2) and (4) apply to the concentrated solutions (15 to 30 per cent Na_2SO_4). Values of v calculated from these equations are given in Tables III and IV and the divergence from the experimental results is given in the columns marked "Obs.-calc." These differences, when plotted against x_2, gave the usual deviation curve by the help of which the values at even concentrations were calculated. In both series it was desirable to have the two equations overlap so that a check on the interpolation calculations might be made.

Table III

Interpolation Data for Calculation of Specific Volumes of Solutions of Na_2SO_4 in 5% H_2SO_4. Check Determinations brought to Same Concentration

x_2	v	v (obs) Final value	v calc. from Eqn. 1	obs.-calc. $\times 10^6$	v calc. from Eqn. 2	obs.-calc. $\times 10^6$
0	0.971981	0.971980	0.971980	0		
	0.971977					
0.9749	0.964771	0.964771	0.964736	35		
1.9559	0.957524	.0957524	0.957448	76		
3.6033	0.945272	0.945272	0.945207	65		
4.8879	0.935658	0.935660	0.935663	−3		
	0.935661					
10.2833	0.895127	0.895127	0.895575	−448	0.895127	0
15.2911	0.858101	0.858101	0.858367	−266	0.858100	1
20.5871	0.820178	0.820178	0.819018	1160	0.820250	−72
23.1243	0.802504	0.802504	0.800167	2337	0.802598	−94

Table IV

Interpolation Data for Calculation of Specific Volumes of Solutions of Na_2SO_4 in 10% H_2SO_4

x_2	v observed	v calc. from Eqn. 3	obs.-calc. $\times 10^6$	v calc. from Eqn. 4	obs.-calc. $\times 10^6$
0	0.943957	0.943957	0		
1.1640	0.935989	0.936018	−29		
2.0758	0.929742	0.929780	−38		
3.3538	0.921022	0.921084	−62		
5.2076	0.908360	0.908441	−81	0.908674	−314
9.9548	0.875974	0.876065	−91	0.875973	− 1
14.2152	0.846954	0.847010	−56	0.847010	-- 56
18.1127	0.820646	0.820428	218	0.820831	−185
22.2873	0.792937	0.791958	979	0.793129	−192
24.9846	0.775372			0.775413	− 41
28.4890	0.752981			0.752617	364

As a check on the interpolations for Series I, a cubic equation was fitted to the results. The deviations were smaller and the equation was useful over the whole range, but the results were exactly the same as those recorded in TableV. The specific volumes at even concentrations of sodium sulphate are given in Tables V and VI.

TABLE V

Specific Volumes of Solutions of Na_2SO_4 in 5% H_2SO_4

x_2	v Equation 1	v Equation 2	v Weighted mean
0	0.971980		0.97198_0
1	0.964589		0.96458_9
2	0.957196		0.95719_8
3	0.949769		0.94977_0
5	0.934814		0.93481_4
10	0.897244	0.897241	0.89724_4
15	0.860226	0.860228	0.86022_8
20	0.824318	0.824313	0.82431_3
23		0.803363	0.80336_3

TABLE VI

Specific Volumes of Solutions of Na_2SO_4 in 10% H_2SO_4

x_2	v Equation 3	v Equation 4	v Weighted mean
0	0.943957		0.94396
1	0.937115		0.93712
2	0.930278		0.93028
3	0.923442		0.92344
5	0.909777	0.909774	0.90978
10	0.875664	0.875664	0.87566
15	0.841619	0.841629	0.84162_5
18	0.821391	0.821402	0.82140
20		0.808047	0.80805
25		0.775274	0.77527
28		0.756084	0.75608
30		0.743428	0.74343

The fictive volumes of Na_2SO_4 in the various solutions may now be calculated, as v_2, the fictive volume of the salt, is given by the equation

$$v_2 = (100-x_2)\, dv/dx_2 + v.$$

Approximate values of dv/dx_2 were found by the differentiation of equations 1, 2, 3 and 4. These approximate values were corrected by adding the slopes of the deviation curves at the appropriate points. The corrected values of dv/dx_2 are recorded in Tables VII and VIII which illustrate the calculations and give the final values of the fictive volumes at even concentrations. The results in Table VII were confirmed from calculations made from the cubic equation which has already been mentioned.

In Table X is shown the agreement between the observed values of the specific volumes of iodine solutions of different concentrations and those calculated from the equation

$$v = 0.65685 - 0.004173x_2$$

It is remarkable that a linear equation applies so exactly over so large a range of concentration. The last column of this table shows the fictive volumes of iodine at various concentrations as calculated by the method already described.

TABLE VII

Calculation of Fictive Volumes of Na_2SO_4 in Solutions containing 5% H_2SO_4

x_2	$dv/dx_2 \times 10^2$ (Eqn. 1)	$dv/dx_2 \times 10^2$ (Eqn. 2)	$dv/dx_2 \times 10^2$ (Weighted mean)	$x_1\, dv/dx_2$	v	v_2
0	0.7372		0.7372	0.7372	0.9720	0.2348
1	0.7391		0 7391	0.7317	0.9646	0.2329
2	0.7410		0.7410	0.7262	0.9572	0.2310
3	0.7441		0.7441	0.7218	0.9498	0.2280
5	0.7508		0.7508	0.7133	0.9348	0 2215
10	0.7466	0.7461	0.7464	0.6718	0.8972	0.2254
15	0.7320	0 7310	0.7310	0.6213	0.8602	0.2389
20	0.7080	0.7105	0.7105	0.5685	0.8243	0.2558
23		0.6960	0.6960	0.5359	0.8034	0.2675
25		0.6862	0 6862	0.5147	0.7897	0.2750

(These are confirmed by results from cubic equation.)

TABLE VIII

Fictive Volumes of Na_2SO_4 in Solutions containing 10% H_2SO_4

x_2	$dv/dx_2 \times 10^2$ (Eqn. 1)	$dv/dx_2 \times 10^2$ (Eqn. 2)	$dv/dx_2 \times 10^2$ (Weighted mean)	$x_1\, dv/dx_2$	v	v_2
0	0.6840		0.6840	0 6840	0 9440	0.2600
1	0.6838		0.6838	0.6770	0.9371	0.2601
2	0.6837		0.6837	0.6700	0.9303	0.2603
3	0.6835		0.6835	0.6630	0 9234	0.2604
5	0.6830	0.6824	0.6827	0.6486	0.9098	0.2612
10	0.6816	0.6822	0.6820	0.6138	0.8757	0.2619
15	0.6795	0.6773	0.6780	0.5763	0.8416	0.2653
18		0.6710	0.6710	0 5502	0.8214	0.2712
20		0.6643	0.6643	0.5314	0.8080	0.2766
25		0.6455	0.6455	0.4841	0.7753	0.2912
28		0.6354	0.6354	0.4575	0.7561	0.2986

TABLE IX

Specific Volumes of Solutions of Iodine in 48.7% KI
Experimental results at 25°

Weight of Iodine	Weight of solution	Concentration per cent (x_2)	Weight of solution in pycnometer	Specific volume (v)
		0	83.7152	0.65744
5.2128	95.4703	5.4601	86.8124	0.63398
12.0908	121.0945	9.9846	89.4644	0.61519
17.9998	120.0390	14.9950	92.6112	0.59428
25.8572	129.2853	20.0001	95.9874	0.57338
33.9294	135.8123	24.9826	99.5953	0.55261
42.0891	141.5455	29.7354	103.3054	0.53276
52.4860	150.1190	34.9629	107.7049	0.51100
58.2987	145.6945	40.014	112.3395	0.48992
67.6814	150.5092	44.9683	117.2967	0.46921
70.2798	146.0359	48.1250	120.6860	0.45604

TABLE X

Observed and Calculated Specific Volumes of Iodine Solutions.
The fictive volumes of iodine in solution

Concentration per cent x_2	v (observed)	v (calculated)	obs.-calc. $\times 10^6$	Fictive volume v_2
5.4601	0.63398	0.63407	−9	
9.9846	0.61519	0.61519	0	0.2396
14.9950	0.59428	0.59428	0	0.2396
20.0001	0.57338	0.57339	−1	0.2395
24.9826	0.55261	0.55260	+1	0.2396
29.7354	0.53276	0.53277	−1	0.2396
34.9629	0.51100	0.51095	+5	0.2396
40.0140	0.48992	0.48988	+4	0.2395
44.9863	0.46921	0.46920	+1	0.2396
48.1250	0.45604	0.45603	+1	0.2396

Discussion of Results

The chief features of interest revealed by a study of the sulphate solutions may be seen in Fig. 1. The specific volume of liquid Na_2SO_4 at room temperature is not known so v_s, the specific volume of solid Na_2SO_4, is used instead of v_0 and its value is 0.375. The expression $(v_s - v_2)$ is plotted as ordinate and the mol fraction of Na_2SO_4 in the solution is abscissa. The mol fraction rather than the weight fraction was used in order to facilitate comparison of equimolal concentrations of different materials. Curve A refers to sodium sulphate in pure water, curve B, to sodium sulphate in the 4.818 per cent H_2SO_4 solution, and curve C, to the salt in the 9.333 per cent solution of sulphuric acid.

The course of curve A is fairly typical of the way in which the fictive volumes of salts in aqueous solutions vary with concentration.[1] The contraction on solution, $(v_s - v_2)$, is greatest at zero concentration and diminishes steadily as the concentration increases. The very high value of $(v_s - v_2)$ in the dilute solutions may be attributed to two causes (a) attraction between the Na_2SO_4 and H_2O molecules and (b) the depolymerization of water which follows as a result of the reduction in the activity of the simple water molecules by the presence of a salt, a process which takes place with decrease in volume.

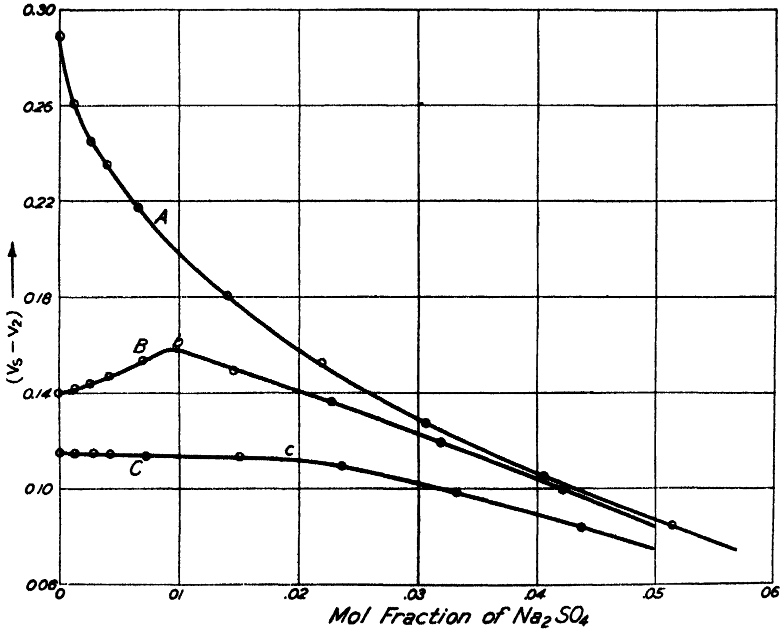

Fig. 1

The differences between the specific volume of solid Na_2SO_4 and the fictive volumes of Na_2SO_4 in solutions in (A) Water, (B) 5 per cent H_2SO_4, (C) 10 per cent H_2SO_4 as functions of the mol fraction of Na_2SO_4 in solution.

Turning to curves B and C we notice that the higher the concentration of sulphuric acid in the solvent, the smaller is the value of $(v_s - v_2)$ at zero concentration. Undoubtedly the addition of sulphuric acid reduces the polymerization of water so that when Na_2SO_4 is added to the solution the contraction due to this effect alone is lessened.

A very interesting question now arises—why do not curves B and C start downward toward the concentration axis at zero concentration as curve A does, and what is the significance of the points b and c where these curves finally do acquire a negative slope. At the point b the mol fraction of H_2SO_4 in the solution is 0.0091 and at c the mol fraction of H_2SO_4 in the solution is 0.018. These figures are approximately the same as the values of the mol fractions of sodium sulphate in the solutions represented by the points b and c. The curves therefore undergo an abrupt change in slope at the points where the solutions contain equimolecular amounts of sodium and hydrogen sulphate or the correct proportions for the production of $NaHSO_4$. It is assumed in explanation that the reaction $Na_2SO_4 + H_2SO_4 \rightarrow 2NaHSO_4$ is accompanied by a decrease in volume and that, as the concentration of Na_2SO_4 rises, the reaction proceeds to an increasing extent reaching a maximum when the two sulphates are present in equimolecular concentration.

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[1] The data for this curve are taken from Gibson: loc. cit.

While it cannot be claimed that the curves in Fig. 1 give absolutely convincing evidence of the compound formation in solution, the case is put forward as an example of some interest where a function derived from an intensive property of the solution as a whole may be linked with the possibility of the compound formation in the solution.

The sulphate results led to an investigation of the question whether this mode of attack might furnish any evidence of the alleged combination of iodine and potassium iodide to form potassium triiodide in solution. The discussion as to what happens in solutions of iodine in aqueous potassium iodide has been admirably summarized by Jones[1] who concluded that the evidence is overwhelmingly in favor of the formation of triiodide. Nevertheless, the results of this investigation cannot be interpreted as giving any evidence in favor of the formation of KI_3; but on the other hand point to the conclusion that if KI_3 is formed it must be in very small amount—which does not agree with figures which are given as the equilibrium constant of the triiodide reaction.

In order to include in the range of experiments a solution in which there should be equimolecular amounts of I_2 and KI it was necessary to employ a very concentrated solution of KI (48.7 per cent). Such a solution would contain equimolecular amounts of I_2 and KI when the concentration of iodine was 42.68 per cent. The last column of Table X shows that over a range of concentrations extending from 10 to 48 per cent of I_2 the fictive volume of iodine in the solution is constant at a value of 0.2396 cc. per gram. There is a complete absence of any singularity around 42.7 per cent. It should be noted that it was not possible to make reliable estimates of v_2 below 10 per cent as an insufficient number of points were observed. The constancy of the fictive volume over this large range of concentration precludes any large interaction between the iodine and the potassium iodide. Data on the specific volume of liquid iodine at 25° are lacking. At 19°C the specific volume of solid iodine is 0.2036.[2] If we assume that iodine expands roughly 10 per cent on melting, the specific volume at 25° of liquid iodine is about 0.22 cc. The specific volume of liquid iodine at 183° is given as 0.2698 by Drugman and Ramsay[3] which leads to an estimate of 0.23 as the specific volume at 25° if the coefficient of expansion of iodine is not far from that of bromine (1.1×10^{-3}). It would seem that v_0, the specific volume of liquefied iodine, is not far from 0.23 at 25°. Hence the value of the expression (v_0-v_2) for iodine in a 48.7 per cent solution of KI is of the order of -0.01 or probably numerically less. The conclusion is that when iodine dissolves in concentrated solutions of iodine in aqueous potassium iodide the volume change is very small, being, if anything, a slight expansion. In other words, from the point of view of volume relations, the concentrated solutions of iodine in aqueous potassium iodide which have been examined approximate closely to a requirement of ideal solutions, namely, that (v_0-v_2) shall be zero at all concentrations. It must be emphasized that in this work only large effects were sought. To investigate the existence of small changes in v_2 it would have been necessary to extend the accuracy of the specific-volume measurements to the sixth decimal place—a task which is particularly difficult with solutions containing a volatile component like iodine. The results given here, however, show that the specific interaction between molecules of iodine and of potassium iodide as measured by volume changes is not appreciably greater and in fact may be less than the interaction of molecules of iodine among themselves in the liquid state.

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[1] Grinnell Jones: J. Phys. Chem., 34, 673 (1930).
[2] "International Critical Tables," 3, 21.
[3] Drugman and Ramsay: J. Chem. Soc., 77, 1228 (1900).

Summary

From measurements of the specific volumes of two series of solutions of sodium sulphate, in the first series approximately 5 per cent aqueous H_2SO_4 and in the second approximately 10 per cent H_2SO_4 being the solvent, the fictive volumes of Na_2SO_4 in these solutions were calculated. The curves showing the relation between a constant minus the fictive volume and the concentration exhibited peculiarities which were linked with the formation of $NaHSO_4$ in solution. Measurements of the specific volumes of iodine in a 49 per cent solution of potassium iodide showed that in solutions containing from 10 to 50 per cent of iodine the fictive volume of the iodine is independent of the concentration of iodine and is close in value to the most probable estimate of the specific volume of liquid iodine at 25°.

Geophysical Laboratory,
Carnegie Institution of Washington,
July, 1930.

STUDIES ON ELECTROKINETIC POTENTIALS. VIII

Ion Antagonism*

BY HENRY B. BULL AND ROSS AIKEN GORTNER

Historical

It has long been recognized by biologists that electrolytes which are individually toxic to cell life are no longer toxic when present in the proper ratios with certain other electrolytes. That this is true has been demonstrated by Loeb,[1] Szück,[2] Berger,[3] Lillie,[4] and others.

Osterhout[5] has shown the existence of ion antagonism between NaCl and $CaCl_2$ by studying the electrical conductance of *Laminaria* tissue in the presence of NaCl and $CaCl_2$ solutions. With NaCl the conductivity of the tissue was increased; with $CaCl_2$ it was decreased. When the salts were present in the ratio of 100 molecules of NaCl to 1 of $CaCl_2$ the conductance of tissue indicated increasing permeability.

Neuschloss[6] reports a marked ion antagonism in the effect on the surface tension of lecithin sols. The alkalies, alkali earths, and aluminum increase the surface tension of lecithin sols to a maximum. This maximum is considerably depressed upon the addition of another electrolyte. He reports that a maximum effect is secured when the ratio of uni-univalent cation mixture is 1:1, uni-bivalent 20:1, and uni-trivalent 100:1. An exception is encountered with Na and K which have their maximum effects in a ratio of Na to K of 1:20 or K to Na of 1:20.

Freundlich and Scholz[7] believe that the ion antagonism encountered in sols in the test tube is closely related to the biological action of electrolytes. It is also their belief that purely electrical influences of pronounced ion antagonism cannot be produced; for ionic antagonism a hydration influence is always necessary.

Weiser[8,9,10,11] has done considerable work on ion antagonism in colloidal systems. He does not agree with Freundlich and Scholz that emphasis should be placed on the hydration influences but maintains rather that the electrical effects play the major role. He seems to feel that there are two factors which influence the precipitating power of a mixture of electrolytes on a colloidal system. These are: (1) the effect of each precipitating ion on the adsorption of the other and (2) the stabilizing action of the ion having the same charge as the colloidal particles. Weiser compares the cell membrane to a copper ferrocyanide membrane. He thinks that the membrane consists of myriads of

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small particles which adsorb water strongly, forming a true colloidal system which is capable of reversible coagulation, and that all the work on the effect of electrolyte mixtures on colloidal systems should apply.

Clowes[12] worked on the problem of emulsion inversion as influenced by different ions. He concludes that the mono-valent cations, in general, favor the oil-in-water emulsion and that di- and tri-valent cations favor the water-in-oil emulsion. There appears to be a marked antagonism between Na and Ca, both in respect to the type of emulsion and their effect upon the interfacial tension of oil-water. NaCl was found to increase the interfacial tension between olive oil and a solution of NaOH or Na oleate or a mixture of both. $CaCl_2$ in the presence of $Ca(OH)_2$ was found to increase the interfacial tension. Here again an ion antagonism was found when the ratio of Ca to Na was 1 to 100. Clowes suggests that the cell membrane is also an emulsion which is capable of inversion, and depending on whether or not we have Ca or Na we get an oil-in-water emulsion which is permeable or a water-in-oil which is impermeable to water-soluble materials. At the proper concentrations Na and Ca ions antagonize each other, and we have an inversion point at which neither type of emulsion predominates.

Harkins and Zollman[13] repeated the work of Clowes in so far as the ion effects upon interfacial tension of oil-water systems are concerned, and using exact physico-chemical technic demonstrated a marked lowering of interfacial tension in pure solutions of NaCl, an increased interfacial tension in pure solutions of $CaCl_2$, and an ion antagonism between Na and Ca so that no changes in interfacial tension occurred in the proper mixtures of NaCl and $CaCl_2$.

Simms[14] reports the effect of neutral salts on the pH of a glycine solution. He finds an ion antagonism between NaCl and KCl; NaCl and $MgCl_2$; NaCl and $CaCl_2$; $CaCl_2$ and $MgCl_2$. The fact that ion antagonism was observed in a non-colloidal system is very suggestive.

Experimental

The apparatus and technic were identical with those of our previous paper[15] and involved only slight modifications from those used by Martin and Gortner[16] which in turn were a modification of Briggs'[17] methods.

Salt	Equivalent ratio	Milli-equivalents per liter	Mg per liter
Na_2SO_4	0.5	0.0075	0.53
Na_2HPO_4	3.0	0.0450	8.06
$NaHCO_3$	30.0	0.4500	37.80
NaCl	89.5	1.3428	78.49
KCl	4.3	0.0645	4.81
$CaCl_2$	3.4	0.0510	3.75
$MgCl_2$	2.6	0.0390	3.96

The dilute physiological salt solution was made up to contain the salts in the same ionic ratios as in blood plasma. The dilutions were made from the stock solutions shown on the preceding page.

The cation concentration of the dilute physiological salt solution in the streaming cell was increased progressively until 0.2×10^{-3} N was reached. At this point sufficient $MgCl_2$ was added to make the solution 0.05×10^{-3} N in respect to Mg and in addition to the amount of Mg already in solution. This solution was streamed through the diaphragm, then sufficient $CaCl_2$ was added to the solution to make it 0.05×10^{-3} N in respect to Ca in addition to that already in solution.

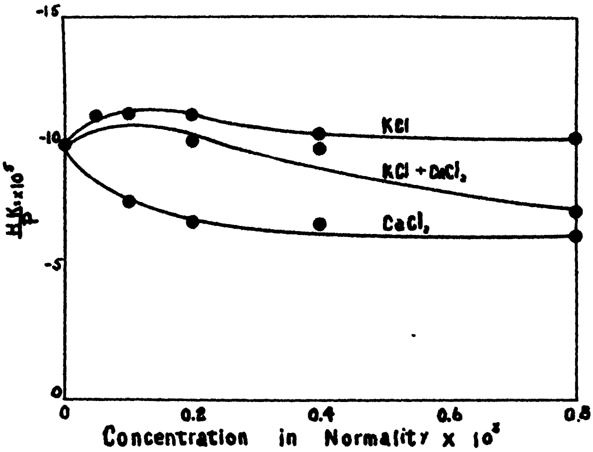

FIG. 1
Showing the effect of KCl and $CaCl_2$ and of mixtures of these salts on H_{κ_s}/P.

The same technic was employed with the K and Na in the ratio of 20:1 and also with the Na and Ca in the ratio of 100:1, as with the dilute physiological salt solution.

The data are given in Tables I to XIV and Figs. 1 through 9. The concentration is always expressed in terms of the total cation equivalency. As with all the results reported in this paper, the individual datum is the average of six determinations, three made while streaming the liquid in one direction and three in the reverse direction. For comparative purposes the data for each curve are multiplied by an appropriate factor so that the value of H_{κ_s}/P for zero salt concentration is reduced to 10×10^{-5}.

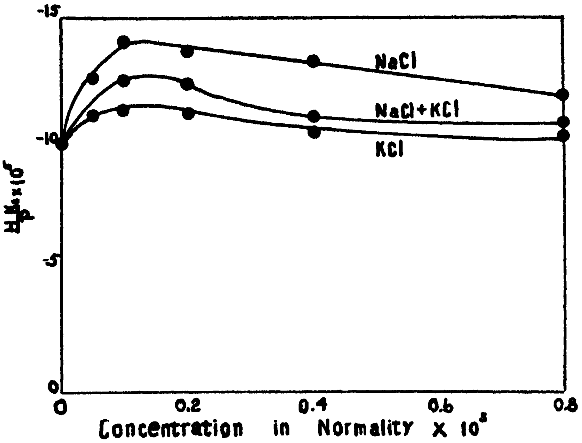

FIG. 2

Showing the effect of NaCl and KCl and of mixtures of these salts on $H\kappa_s/P$.

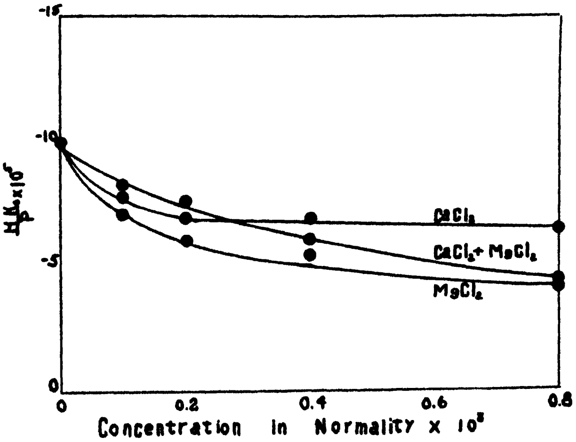

FIG. 3

Showing the effect of $CaCl_2$ and $MgCl_2$ and of mixtures of these salts on $H\kappa_s/P$.

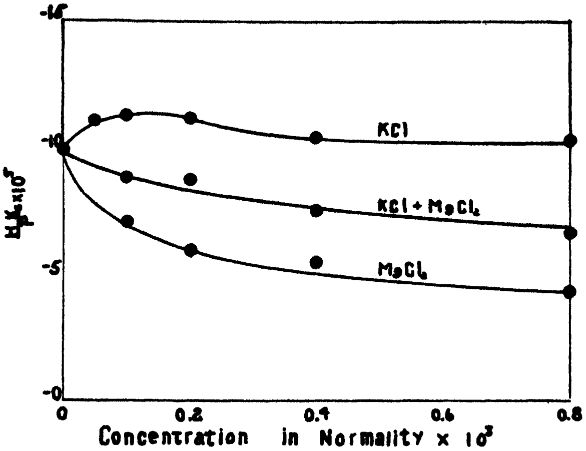

FIG. 4

Showing the effect of $MgCl_2$ and KCl and of mixtures of these salts on H_{K_s}/P.

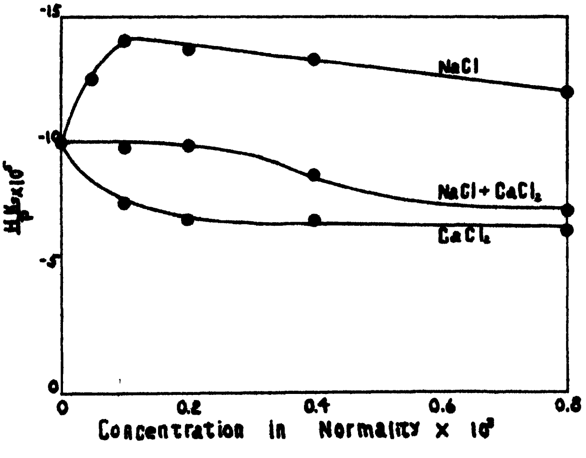

FIG. 5

Showing the effect of NaCl and $CaCl_2$ and of mixtures of these salts on H_{K_s}/P.

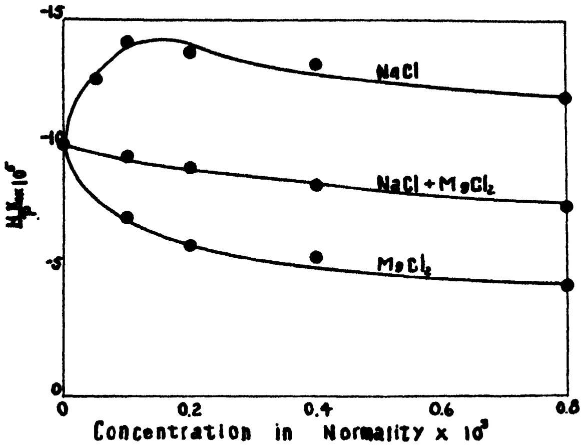

Fig. 6

Showing the effect of NaCl and MgCl₂ and of mixtures of these salts on H_{K_s}/P.

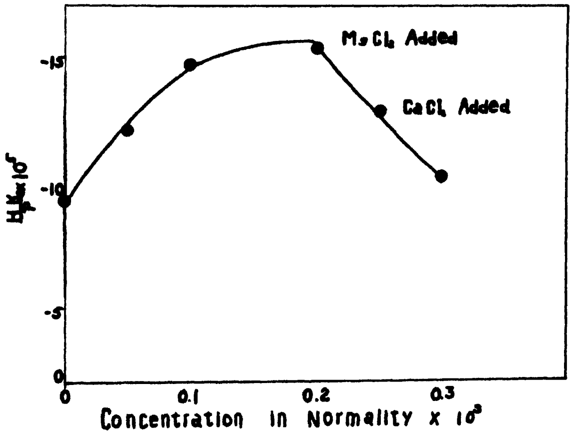

Fig. 7

Showing the effect of MgCl₂ and CaCl₂ upon the ζ-potential in a dilute physiological salt solution.

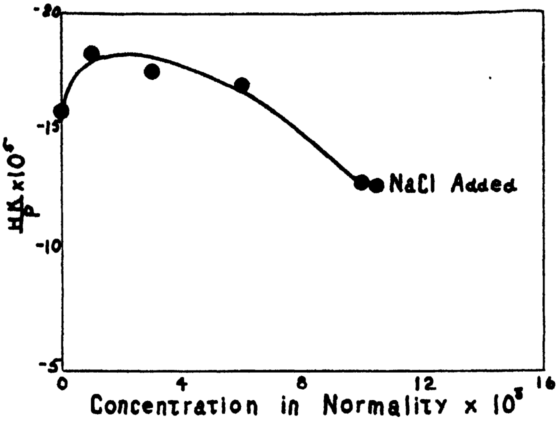

Fig. 8

Showing the effect of the addition of NaCl to KCl in the ratio of 1 to 20 on the electrical potential at a cellulose-aqueous interface.

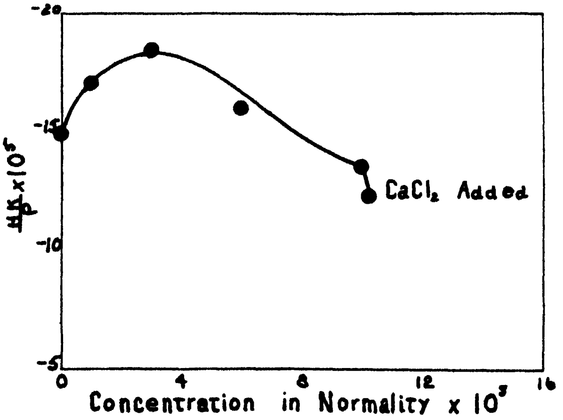

Fig. 9

Showing the effect of the addition of $CaCl_2$ to NaCl in the molecular ratio of 1 to 100 on the electrical potential at a cellulose-aqueous interface.

TABLE I

Data for $MgCl_2$

Concentration $MgCl_2$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10$
0.00	61.3	−15.5	57.2	−15.5
	78.1	−15.5	79.6	−15.5
	75.5	−15.5	78.3	−15.3
		Average $H\kappa_s/P = -15.48 \times 10^{-5}$		
0.10×10^{-3}	66.3	−10.5	74.5	−11.4
	80.9	−11.1	81.7	−11.1
	73.9	−11.5	75.7	−10.7
		Average $H\kappa_s/P = -11.05 \times 10^{-5}$		
0.20×10^{-3}	51.2	− 8.52	58.9	− 8.84
	80.6	− 9.95	80.6	− 9.42
	78.5	− 9.76	78.9	− 9.45
		Average $H\kappa_s/P = -9.32 \times 10^{-5}$		
0.4×10^{-3}	60.5	− 8.83	63.0	− 8.05
	80.9	− 8.72	81.4	− 8.50
	79.5	− 8.60	79.3	− 8.24
		Average $H\kappa_s/P = -8.50 \times 10^{-5}$		
0.8×10^{-3}	50.1	− 6.90	61.8	− 5.10
	80.6	− 6.94	81.3	− 6.75
	76.5	− 6.68	78.1	− 6.52
		Average $H\kappa_s/P = -6.75 \times 10^{-5}$		
1.6×10^{-3}	81.9	− 2.69	66.9	− 3.10
	80.7	− 2.00	81.1	− 2.71
		Average $H\kappa_s/P = -2.62 \times 10^{-5}$		

TABLE II

Data for $CaCl_2$

Concentration $CaCl_2$	Pressure cm. Hg	$\frac{H_{\kappa_s}}{P} \times 10^5$	Pressure cm. Hg	$\frac{H_{\kappa_s}}{P} \times 10^5$
0.00	77.2	−13.7	68.3	−13.4
	72.0	−13.8	72.9	−13.6
	69.5	−14.0		
		Average $H\kappa_s/P = -13.7 \times 10^{-5}$		
0.1×10^{-3}	63.5	−10.5	51.8	−11.6
	74.9	−10.4	73.7	−10.5
			78.4	−10.5
		Average $H\kappa_s/P = -10\ 7 \times 10^{-5}$		
0.2×10^{-3}	53.8	− 9.80	57.9	−10.1
	76.9	− 9.45	76.9	− 9.4
	82.3	− 9.20	82.9	− 9 3
		Average $H\kappa_s/P = -9\ 55 \times 10^{-5}$		
0.4×10^{-3}	80.3	− 9.2	52.2	−10.8
	82.8	− 9.3	73.1	− 9.5
	75.5	− 9.2	80.4	− 9.2
		Average $H\kappa_s/P = -9.55 \times 10^{-5}$		
0.8×10^{-3}	59.0	−10.0	66.0	− 9.5
	78.2	− 8.9	80.2	− 8.5
	83.5	− 8.0	82.9	− 8.4
		Average $H\kappa_s/P = -8.90 \times 10^{-5}$		
1.6×10^{-3}	70.5	− 9.0	67.8	− 9.5
	79.0	− 8.8	80.3	− 8.6
	82.3	− 8.7	76.4	− 8.6
		Average $H\kappa_s/P = -8.87 \times 10^{-5}$		

TABLE III

Data for KCl

Concentration KCl	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
0.00	51.9	−13.0	51.6	−11.5
	78.4	−12.6	83.0	−12.4
			78.2	−12.6
		Average $H\kappa_s/P = -12.4 \times 10^{-5}$		
0.05×10^{-3}	77.4	−13.8	80.6	−13.8
	82.4	−13.8	77.2	−13.8
	76.0	−13.6		
		Average $H\kappa_s/P = -13.8 \times 10^{-5}$		
0.10×10^{-3}	48.7	−15.1	59.1	−12.4
	82.2	−14.3	77.4	−14.1
	76.1	−14.3	84.4	−14.2
		Average $H\kappa_s/P = -14.01 \times 10^{-5}$		
0.20×10^{-3}	36.7	−13.7	63.3	−13.1
	79.0	−14.3	82.4	−14.2
	85.5	−13.9	78.2	−14.4
		Average $H\kappa_s/P = -13.9 \times 10^{-5}$		
0.4×10^{-3}	81.2	−12.7	50.3	−12.50
	66.8	−12.4	82.9	−12.95
	71.4	−13.5	72.2	−13.40
		Average $H\kappa_s/P = -12.9 \times 10^{-5}$		
0.8×10^{-3}	41.6	−11.75	53.2	−13.7
	76.7	−12.3	76.8	−12.6
	83.3	−12.2	68.7	−13.4
		Average $H\kappa_s/P = -12.8 \times 10^{-5}$		

TABLE IV

Data for NaCl

Concentration NaCl	Pressure cm. Hg	$\frac{H_{\kappa_s}}{P} \times 10^5$	Pressure cm. Hg	$\frac{H_{\kappa_s}}{P} \times 10^5$
0.00	71.9	−10.23	75.9	− 9.85
	75.1	− 9.90	79.1	− 9.70
	78.9	−10.02	72.0	− 9.70
		Average $H_{\kappa_s}/P = -9.90 \times 10^{-5}$		
0.05×10^{-3}	70.3	−12.80	69.7	−12.84
	78.5	−12.34	74.7	−12.50
	73.9	−12.45	78.6	−12.58
		Average $H_{\kappa_s}/P = -12.6 \times 10^{-5}$		
0.10×10^{-3}	72.9	−13.90	74.1	−14.30
	75.7	−13.85	76.5	−14.40
	79.7	−13.70	73.5	−15.50
		Average $H_{\kappa_s}/P = -14.1 \times 10^{-5}$		
0.2×10^{-3}	71.3	−14.0	72.9	−13.8
	75.1	−13.8	75.9	−13.6
	79.0	−13.7	79.2	−13.6
		Average $H_{\kappa_s}/P = -13.75 \times 10^{-5}$		
0.4×10^{-3}	69.5	−13.4	73.2	−13.3
	74.7	−13.4	76.9	−13.0
	78.3	−13.5	80.2	−13.1
		Average $H_{\kappa_s}/P = -13.30 \times 10^{-5}$		
0.8×10^{-3}	61.5	−12.40	71.7	−11.6
	70.1	−12.45	75.7	−11.6
	77.7	−12.35	82.1	−11.2
		Average $H_{\kappa_s}/P = -11.95 \times 10^{-5}$		
1.6×10^{-3}	67.8	−10.02	75.2	−11.6
	74.8	−10.20	79.2	−11.6
	80.5	−10.25	82.3	−11.8
		Average $H_{\kappa_s}/P = -10.90 \times 10^{-5}$		

TABLE V

Data for $MgCl_2$ and $CaCl_2$ in 1:1 ratio

Concentration		Pressure	$\frac{H\kappa_s}{P} \times 10^5$	Pressure	$\frac{H\kappa_s}{P} \times 10^5$
$MgCl_2$	$CaCl_2$	cm. Hg		cm. Hg	
0.00	0.00	73.3	−12.45	71.6	−11.82
		71.4	−12.20	80.7	−12.20
		77.4	−12.26	74.0	−12.40
			Average $H\kappa_s/P = -12.2 \times 10^{-5}$		
$0.05 \times 10^{-3}N$	$0.05 \times 10^{-3}N$	72.7	−10.6	62.2	−11.0
		81.3	− 9.9	74.6	− 9.9
		76.3	− 9.7		
			Average $H\kappa_s/P = -10.22 \times 10^{-5}$		
$0.1 \times 10^{-3}N$	$0.1 \times 10^{-3}N$	53.4	− 9.16	59.5	− 9.70
		63.4	− 9.20	74.0	− 9.32
		66.7	− 9.25	70.8	− 9.25
			Average $H\kappa_s/P = -9.32 \times 10^{-5}$		
$0.2 \times 10^{-3}N$	$0.2 \times 10^{-3}N$	68.3	− 7.26	70.7	− 6.85
		74.4	− 7.85	76.7	− 7.50
		69.9	− 7.62	70.0	− 7.62
			Average $H\kappa_s/P = -7.45 \times 10^{-5}$		
$0.4 \times 10^{-3}N$	$0.4 \times 10^{-3}N$	54.9	− 5.20	62.1	− 4.37
		69.1	− 5.95	70.6	− 5.72
		82.8	− 6.12	84.0	− 5.42
			Average $H\kappa_s/P = -5.46 \times 10^{-5}$		
$0.8 \times 10^{-3}N$	$0.8 \times 10^{-3}N$	75.3	− 3.38	56.8	− 4.85
		79.7	− 4.83	82.4	− 5.10
		82.0	− 5.12	78.2	− 5.06
			Average $H\kappa_s/P = -4.72 \times 10^{-5}$		

TABLE VI

Data for Mixture of $MgCl_2$ and KCl in Equivalent Ratio of 1:1

Concentration					
$MgCl_2$	KCl	Pressure cm. Hg	$\frac{H_{\kappa_s}}{P} \times 10^5$	Pressure cm. Hg	$\frac{H_{\kappa_s}}{P} \times 10^5$
0.00	0.00	52.0	−13.20	61.9	−12.30
		69.9	−13.35	69.4	−13.37
		82.3	−13.18	81.8	−13.75
			Average $H_{\kappa_s}/P = -13.2 \times 10^{-5}$		
$0.05 \times 10^{-3}N$	$0.05 \times 10^{-3}N$	64.1	−11.8	45.9	−10.2
		79.1	−12.3	66.3	−11.7
		76.0	−12.4	81.2	−12.3
			Average $H_{\kappa_s}/P = -11.8 \times 10^{-5}$		
$0.10 \times 10^{-3}N$	$0.10 \times 10^{-3}N$	56.8	−11.1	62.2	−11.5
		69.2	−11.8	81.4	−11.6
		79.6	−11.9	82.3	−12.3
			Average $H_{\kappa_s}/P = -11.7 \times 10^{-5}$		
$0.2 \times 10^{-3}N$	$0.20 \times 10^{-3}N$	49.6	− 9.80	64.7	− 8.50
		78.8	−10.40	78.2	−10.30
		83.1	−10.50	81.9	−10.60
			Average $H_{\kappa_s}/P = -10.0 \times 10^{-5}$		
$0.40 \times 10^{-3}N$	$0.40 \times 10^{-3}N$	60.7	− 9.00	65.9	− 7.94
		78.5	− 9.00	80.3	− 9.00
		81.3	− 9.15	75.2	− 9.10
			Average $H_{\kappa_s}/P = -8.86 \times 10^{-5}$		
$0.80 \times 10^{-3}N$	$0.80 \times 10^{-3}N$	59.1	− 5.95	78.2	− 7.20
		81.9	− 7.60	82.7	− 7.60
		77.1	− 8.45	75.1	− 8.05
			Average $H_{\kappa_s}/P = -7.48 \times 10^{-5}$		

TABLE VII

Data for Mixture of $CaCl_2$ and KCl in Equivalent Ratio of 1:1

Concentration		Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
$CaCl_2$	KCl				
0.00	0.00	77.2	−11.10	82.6	− 9.10
		81.4	−11.10	86.7	− 9.12
		86.0	−11.10	76.4	− 9.05
			Average $H\kappa_s/P = -10.1 \times 10^{-5}$		
$0.05 \times 10^{-3}N$	$0.05 \times 10^{-3}N$	75.6	−11.3	80.2	−11.42
		80.5	−11.2	84.7	−11.50
		85.0	−11.0	75.1	−11.97
			Average $H\kappa_s/P = -11.4 \times 10^{-5}$		
$0.1 \times 10^{-3}N$	$0.1 \times 10^{-3}N$	78.8	−10.18	81.1	−10.12
		82.4	−10.05	86.2	−10.13
		86.6	−10.03	72.8	−10.50
			Average $H\kappa_s/P = -10.15 \times 10^{-5}$		
$0.2 \times 10^{-3}N$	$0.2 \times 10^{-3}N$	68.5	− 9.77	79.8	− 9.22
		77.7	−10.00	85.6	− 9.60
		85.2	−10.22	72.0	−10.17
			Average $H\kappa_s/P = -9.83 \times 10^{-5}$		
$0.4 \times 10^{-3}N$	$0.4 \times 10^{-3}N$	85.8	− 7.73		
		81.0	− 7.70		
		73.4	− 7.85		
			Average $H\kappa_s/P = -7.76 \times 10^{-5}$		

TABLE VIII

Data for Mixture of NaCl and $MgCl_2$ in Equivalent Ratio of 1:1

Concentration		Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
NaCl	$MgCl_2$				
0.00	0.00	72.7	−11.20	81.0	−10.00
		79.6	−11.34	84.1	− 9.95
		85.5	−11.38	87.4	−10.32
			Average $H\kappa_s/P = -10.7 \times 10^{-5}$		

TABLE VIII (Continued)

Data for Mixture of NaCl and $MgCl_2$ in Equivalent Ratio of 1:1

Concentration NaCl	Concentration $MgCl_2$	Pressure	$\frac{H_{K_s}}{P} \times 10^5$	Pressure	$\frac{H_{K_s}}{P} \times 10^5$
0.05×10^{-3}N	0.05×10^{-3}N	71.9	−10.25	81.8	−10.28
		79.9	−10.22	84.0	−10.27
		85.1	−10.28	76.8	−10.00
			Average $H_{K_s}/P = -10.22 \times 10^{-5}$		
0.1×10^{-3}N	0.1×10^{-3}N	74.8	− 9.75	74.9	− 9.60
		80.9	− 9.75	81.2	− 9.60
		84.8	−10.00	86.1	− 9.60
			Average $H_{K_s}/P = -9.75 \times 10^{-5}$		
0.2×10^{-3}N	0.2×10^{-3}N	79.1	− 9.15	81.8	− 8.90
		82.5	− 9.07	87.0	− 8.86
		86.8	− 9.15	77.7	− 9.20
			Average $H_{K_s}/P = -9.05 \times 10^{-5}$		
0.4×10^{-3}N	0.4×10^{-3}N	74.0	− 8.12	80.6	− 8.05
		80.5	− 8.23	84.1	− 7.96
		86.0	− 8.26	88.5	− 7.82
			Average $H_{K_s}/P = -8.07 \times 10^{-5}$		
0.8×10^{-3}N	0.8×10^{-3}N	72.4	− 6.27	80.6	− 6.62
		79.7	− 6.30	86.0	− 7.02
		86.1	− 6.25	75.6	− 6.90
			Average $H_{K_s}/P = -6.55 \times 10^{-5}$		

TABLE IX

Data for Mixture of NaCl and $CaCl_2$ in Equivalent Ratio of 1:1

Concentration NaCl	Concentration $CaCl_2$	Pressure cm. Hg	$\frac{H_{K_s}}{P} \times 10^5$	Pressure cm. Hg	$\frac{H_{K_s}}{P} \times 10^5$
0.00	0.00	66.1	− 9.90	63.5	−10.00
		76.5	−10.00	70.0	− 9.75
		79.3	− 9.90	74.8	− 9.65
			Average $H_{K_s}/P = -9.86 \times 10^{-5}$		
0.05×10^{-3}N	0.05×10^{-3}N	58.4	−10.35	51.5	− 9.48
		68.9	−10.23	63.8	− 9.02
		73.7	−10.20	70.9	− 9.10
			Average $H_{K_s}/P = -9.72 \times 10^{-5}$		

TABLE IX (Continued)

Data for Mixture of NaCl and $CaCl_2$ in Equivalent Ratio of 1:1

Concentration NaCl	 $CaCl_2$	Pressure	$\frac{H\kappa_s}{P} \times 10^5$	Pressure	$\frac{H\kappa_s}{P} \times 10^5$
0.1×10^{-3}N	0.1×10^{-3}N	41.1	− 9.75	48.1	− 9.84
		60.9	− 9.62	73.7	− 9.65
		69.5	− 9.72	68.3	− 9.70
			Average $H\kappa_s/P = -9.71 \times 10^{-5}$		
0.2×10^{-3}N	0.2×10^{-3}N	67.8	− 8.35	62.8	− 8.65
		58.1	− 8.33	70.7	− 8.76
				69.9	− 8.78
			Average $H\kappa_s/P = -8.57 \times 10^{-5}$		
0.4×10^{-3}N	0.4×10^{-3}N	66.9	− 7.90	75.0	− 7.20
		75.0	− 7.75	79.8	− 6.67
		78.2	− 7.80	69.1	− 5.64
			Average $H\kappa_s/P = -7.15 \times 10^{-5}$		
0.8×10^{-3}N	0.8×10^{-3}N	70.9	− 6.13	77.3	− 6.07
		76.9	− 6.10	81.4	− 6.33
		80.3	− 6.15	60.5	− 6.63
			Average $H\kappa_s/P = -6.24 \times 10^{-5}$		

TABLE X

Data for Mixture of NaCl and KCl in Equivalent Ratio of 1:1

Concentration NaCl	 KCl	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$	Pressure cm. Hg	$\frac{H\kappa_s}{P} \times 10^5$
0.00	0.00	59.9	−12.3	48.9	−10.7
		77.5	−11.9	78.8	−11.9
		78.3	−11.8	81.1	−12.3
			Average $H\kappa_s/P = -11.8 \times 10^{-5}$		
0.05×10^{-3}N	0.05×10^{-3}N	61.7	−14.7	53.4	−14.6
		78.9	−14.8	82.1	−14.9
		82.8	−14.6	79.2	−15.1
			Average $H\kappa_s/P = -14.8 \times 10^{-5}$		

TABLE X (Continued)

Data for Mixture of NaCl and KCl in Equivalent Ratio of 1:1

Concentration NaCl	Concentration KCl	Pressure	$\frac{H_{K_s}}{P} \times 10^5$	Pressure	$\frac{H_{K_s}}{P} \times 10^5$
$0.10 \times 10^{-3}N$	$0.10 \times 10^{-3}N$	62.5	−14.5	59.1	−13.4
		78.1	−14.5	77.5	−14.6
		82.3	−14.6	71.2	−16.5
			Average $H_{K_s}/P = -14.7 \times 10^{-5}$		
$0.20 \times 10^{-3}N$	$0.20 \times 10^{-3}N$	78.0	−12.90	54.4	−10.90
		80.0	−13.05	81.0	−12.90
		77.6	−13.00	81.4	−13.30
			Average $H_{K_s}/P = -13.03 \times 10^{-5}$		
$0.4 \times 10^{-3}N$	$0.40 \times 10^{-3}N$	52.2	−13.00	54.1	−12.30
		78.8	−12.80	78.6	−12.90
		82.8	−12.85	81.2	−12.60
			Average $H_{K_s}/P = -12.72 \times 10^{-5}$		
$0.8 \times 10^{-3}N$	$0.8 \times 10^{-3}N$	65.4	− 8.55	54.2	− 7.20
		81.2	− 9.98	82.0	− 9.95
		81.8	− 9.70	84.2	−10.25
			Average $H_{K_s}/P = -9.27 \times 10^{-5}$		

TABLE XI

Summary of Ion Antagonism Data

$H_{K_s}/P \times 10^5$

Concentration in Cation Equiv.	$MgCl_2$	$CaCl_2$	NaCl	KCl
0.00	−15.48	−13.70	− 9.90	−12.4
0.05×10^{-3}			−12.60	−13.8
0.10×10^{-3}	−11.05	−10.70	−14.10	−14.01
0.20×10^{-3}	− 9.32	− 9.55	−13.75	−13.9
0.40×10^{-3}	− 8.50	− 9.55	−13.30	−12.9
0.80×10^{-3}	− 6.76	− 8.90	−11.95	−12.8
1.60×10^{-3}	− 2.62	− 8.87	−10.90	−13.6

	$MgCl_2$ $CaCl_2$	$MgCl_2$ KCl	$MgCl_2$ NaCl	$CaCl_2$ KCl	$CaCl_2$ NaCl	KCl NaCl
0.00	−12.2	−13.20	−10.70	−10.10	−9.86	−11.80
0.05×10^{-3}						
0.10×10^{-3}	−10.2	−11.80	−10.22	−11.40	−9.72	−14.80
0.20×10^{-3}	− 9.32	−11.70	− 9.75	−10.15	−9.71	−14.70
0.40×10^{-3}	− 7.45	−10.00	− 9.05	− 9.83	−8.57	−13.03
0.80×10^{-3}	− 5.46	− 8.86	− 8.07	− 7.76	−7.15	−12.72
1.60×10^{-3}	− 4.72	− 7.48	− 6.55		−6.24	− 9.27

TABLE XII

Data for Dilute Physiological Salt Mixture

Cation concentration $\times 10^3$	Pressure cm. Hg	H/P	Pressure cm. Hg	H/P
0.0	82.7	−3.911	82.5	−3.860
	84.9	−3.904	84.8	−3.879
	86.8	−3.934	86.2	−3.915
	Average H/P = −3.900	$H\kappa_s/P = -9.75 \times 10^{-5}$		
0.05	77.6	−3.279	73.3	−3.342
	81.6	−3.290	78.3	−3.339
	84.9	−3.303	83.8	−3.323
	Average H/P = −3.312	$H\kappa_s/P = -12.57 \times 10^{-5}$		
0.10	82.5	−3.060	83.9	−3.116
	84.1	−3.049	85.0	−3.094
	86.1	−3.072	86.2	−3.091
	Average H/P = −3.08	$H\kappa_s/P = -15.172 \times 10^{-5}$		
0.20	75.5	−2.304	82.4	−2.326
	80.0	−2.287	84.6	−2.304
	85.2	−2.300	86.2	−2.302
	Average H/P = − 2.305	$H\kappa_s/P = -15.85 \times 10^{-5}$		
0.20*	81.0	−1.629	83.6	−1.590
	83.35	−1.625	85.1	−1.603
	87.1	−1.618	86.8	−1.624
	Average H/P = −1.6148	$H\kappa_s/P = -13.29 \times 10^{-5}$		
0.20**	81.7	−1.187	73.0	−1.205
	84.7	−1.186	78.5	−1.223
	88.5	−1.163	83.9	−1.269
	Average H/P = −1.205	$H\kappa_s/P = -10.73 \times 10^{-5}$		

* plus 0.05 × 10^{-3} N $MgCl_2$

** plus 0.05 × 10^{-3} N $MgCl_2$ and 0.05 × 10^{-3} N $CaCl_2$

TABLE XIII

Data for Mixture of NaCl and KCl in the Equivalent Ratio of 1:20

Concentration	Pressure cm. Hg	H/P	Pressure cm. Hg	H/P
0.0	48.6	−6.759	66.5	−6.661
	65.1	−6.589	73.5	−6.639
	73.7	−6.499	79.7	−6.637
Average H/P = −6.6306		$H\kappa_s/P = -15.93 \times 10^{-5}$		
0.1×10^{-3} KCl	58.3	−3.927	70.8	−3.707
	69.6	−3.829	77.7	−3.758
	78.3	−3.767	81.6	−3.792
Average H/P = −3.796		$H\kappa_s/P = -18.38 \times 10^{-5}$		
0.3×10^{-3} KCl	62.5	−2.008	63.7	−1.781
	73.7	−1.953	73.4	−1.744
	80.1	−1.953	80.7	−1.753
Average H/P = −1.8653		$H\kappa_s/P = -17.65 \times 10^{-5}$		
0.6×10^{-3} KCl	65.1	−1.105	65.9	−1.107
	66.0	−1.038	73.9	−1.123
			79.7	−1.122
Average H/P = −1.099		$H\kappa_s/P = -17.06 \times 10^{-5}$		
1.0×10^{-3} KCl Series 1	61.9	−0.5573	62.7	−0.6060
	72.5	−0.5448	70.6	−0.6232
	77.7	−0.5469	78.0	−0.5897
	66.5	−0.6165	66.4	−0.5120
	76.5	−0.5424	74.6	−0.5160
	80.7	−0.5452	80.1	−0.4931
Average H/P = −0.5577		$H\kappa_s/P = -12.715 \times 10^{-5}$		
1.0×10^{-3} KCl Series 2	63.0	−0.5555	64.8	−0.6327
	72.1	−0.5200	71.5	−0.6573
	78.4	−0.5165	80.1	−0.6054
	71.3	−0.5539	70.5	−0.5957
	77.1	−0.5317	76.4	−0.6020
	81.7	−0.5263	81.8	−0.5806
Average H/P = −0.5731		$H\kappa_s/P = -13.18 \times 10^{-5}$		
1.0×10^{-3} KCl $.05 \times 10^{-3}$ NaCl	62.3	−0.5698	66.4	−0.5195
	71.2	−0.5758	75.0	−0.5066
	79.3	−0.5674	81.2	−0.4987
	60.7	−0.5848	67.9	−0.5301
	70.3	−0.5832	75.6	−0.5555
	77.3	−0.5821	80.4	−0.5534
Average H/P = −0.5522		$H\kappa_s/P = -12.75 \times 10^{-5}$		

TABLE XIV

Data for Mixture of NaCl and $CaCl_2$ in Molecular Ratio of 1:100

Concentration	Pressure cm. Hg	H/P	Pressure cm. Hg	H/P
0.0	71.9	−7.065	66.0	−6.636
	78.1	−6.888	75.4	−6.446
	76.2	−6.797	80.7	−6.332
Average H/P = −6.694		$H\kappa_s/P = -14.95 \times 10^{-5}$		
0.1×10^{-3} NaCl	75.4	−3.872	74.5	−3.369
	79.3	−3.883	78.7	−3.437
	82.7	−3.863	83.2	−3.383
Average H/P = −3.634		$H\kappa_s/P = -17.116 \times 10^{-5}$		
0.3×10^{-3} NaCl	71.7	−2.280	67.3	−2.184
	77.1	−2.243	76.9	−2.197
	82.3	−2.205	81.3	−2.195
Average H/P = −2.2173		$H\kappa_s/P = -18.49 \times 10^{-5}$		
0.6×10^{-3} NaCl	58.1	−1.187	68.1	−1.167
	68.5	−1.168	76.3	−1.186
	78.5	−1.133	80.9	−1.162
Average H/P = −1.1671		$H\kappa_s/P = -15.979 \times 10^{-5}$		
1.0×10^{-3} NaCl	70.1	−0.6704	69.7	−0.7317
	75.7	−0.6472	74.1	−0.7422
	80.1	−0.6367	78.4	−0.7716
	68.0	−0.7058	65.9	−0.7132
	74.7	−0.6827	74.5	−0.6711
	79.4	−0.7052	81.0	−0.6666
Average H/P = −0.6953		$H\kappa_s/P = -13.63 \times 10^{-5}$		
1.0×10^{-3} NaCl	63.1	−0.6814	69.5	−0.6906
0.02×10^{-3} $CaCl_2$	73.1	−0.6429	76.2	−0.6692
	80.6	−0.5955	80.5	−0.6708
	84.0	−0.6666	70.5	−0.6241
	74.6	−0.6300	76.1	−0.6438
	81.7	−0.6609	81.7	−0.6365
Average H/P = −0.6510		$H\kappa_s/P = -12.317 \times 10^{-5}$		

Discussion

The results show, in general, an averaged effect of the individual salts in a mixed salt solution upon the surface potential. Thus the curve for KCl and NaCl is clearly simply a component curve of the individual curves for KCl and NaCl. There is a slight suggestion of antagonism between $CaCl_2$ and $MgCl_2$ below a concentration of 0.2×10^{-3}, but it is very doubtful if the results are clear enough to warrant one considering that this is a case of ion antagonism. In any event, it is certainly very slight. Other than this, somewhat doubtful case, we may state definitely that in the concentrations investigated there are no ion antagonistic effects on the surface potential.

The results with dilute physiological salt solution indicate clearly the absence of ion antagonism between $MgCl_2$ and $CaCl_2$, as influencing the electrokinetic potential.

In interpreting these results it is to be remembered that the concentrations used are very much less than those usually employed in observing ion antagonism in biological systems. These low concentrations were necessarily employed since the specific conductivity becomes large in more concentrated solutions and thus invalidates streaming potential measurements.

Summary

1. The surface potential at a cellulose-aqueous solution interface has been measured for solutions of NaCl, KCl, $CaCl_2$, $MgCl_2$, NaCl with KCl, NaCl with $CaCl_2$, NaCl with $MgCl_2$, KCl with $CaCl_2$, KCl with $MgCl_2$, and $CaCl_2$ with $MgCl_2$ up to a total cation normality of 0.8×10^{-3}.

2. With the possible exception of $CaCl_2$ and $MgCl_2$ the results obtained for the mixtures of the salts are more or less an average of the results obtained for the salts separately.

3. There is no antagonism between $MgCl_2$ and $CaCl_2$ in a 0.2×10^{-3} N diluted physiological salt solution.

4. There is no antagonism, as affecting the electrokinetic potential, between KCl and NaCl in the ratio of 20:1, or between NaCl and $CaCl_2$ in the molecular ratio of 100:1.

Literature Cited

[1] J. Loeb: "Artificial Parthenogenesis and Fertilization," (1913).

[2] J. Szück: Experimentelle Beiträge zu einer Theorie der antagonistischen Ionenwirkungen, Jahr. Bot., **52**, 85-142 (1913).

[3] Eva Berger: Unterschiedliche Wirkungen gleicher Ionen und Ionengemische auf verschiedene Tierarten, Pflügers' Archiv, **223**, 1-39 (1929).

[4] Ralph S. Lillie, The Relation of Ions to Ciliary Movement, Am. J. Physiol., **10**, 419-443 (1904).

[5] W. J. V. Osterhout: "Injury, Recovery, and Death, in Relation to Conductivity and Permeability" (1922).

[6] S. M. Neuschloss: Untersuchungen über antagonistische Wirkungen zwischen Ionen gleicher Ladung, Kolloid-Z., **27**, 292-306 (1920).

[7] H. Freundlich and P. Scholz: Über die Flockung durch Elektrolytgemische, Kolloidchem. Beihefte, **16**, 267-284 (1922).

[8] H. B. Weiser: Adsorption by Precipitates. VI., J. Phys. Chem., **28**, 232-244 (1924).

[9] H. B. Weiser: The Antagonistic Action of Ions in the Neutralization of Sols, J. Phys. Chem., **30**, 20-33 (1926).

[10] H. B. Weiser: The Antagonistic Actions of Ions in the Neutralization of Sols II., J. Phys. Chem., **30**, 1527-1537 (1926).

[11] H. B. Weiser: Ionic Antagonism in Colloid Systems, Colloid Symposium Monograph, 4, 354-373 (1926).

[12] G. H. A. Clowes: Protoplasmic Equilibrium. I. Action of Antagonistic Electrolytes on Emulsions and Living Cells, J. Phys. Chem., **20**, 407-451 (1916).

[13] W. D. Harkins and H. Zollman: Interfacial Tension and Emulsification. I. The Effect of Bases, Salts, and Acids upon the Interfacial Tension between Aqueous Sodium Oleate Solutions and Benzene. II. Extremely Small Interfacial Tensions Produced by Solutes, J. Am. Chem. Soc., **48**, 69-80 (1926).

[14] H. S. Simms: Chemical Antagonism of Ions. IV. Effect of Salt Mixtures on Glycine Activity, J. Gen. Physiol., **12**, 783-792 (1929).

[15] H. B. Bull and R. A. Gortner: Studies on Electrokinetic Potentials. VI. Electrical Phenomena at Interfaces, Eighth Colloid Symposium Annual, J. Phys. Chem., **35**, January issue (1931).

[16] W. McK. Martin and R. A. Gortner: Studies on Electrokinetic Potentials, V. Interfacial Energy and the Molecular Structure of Organic Compounds. I. Electrokinetic Potentials at Cellulose-Organic Liquid Interfaces, J. Phys. Chem., **34**, 1509-1539 (1930).

[17] D. R. Briggs: The Determination of the ζ-Potential on Cellulose—A Method, J. Phys. Chem., **32**, 641-675 (1928).

THE DIRECT MEASUREMENT OF THE ADSORPTION OF SOLUBLE SUBSTANCES BY THE BUBBLE METHOD[*]

BY DAVID M. GANS AND WILLIAM D. HARKINS

1. Introduction

While there is conclusive evidence that practically all true films of insoluble substances on water are monomolecular, it is possible that with some soluble substances the amount in the surface corresponds to a polymolecular film. However, the values calculated from the adsorption equation in its "corrected form"

$$u = -\frac{1}{RT}\,\frac{\delta\gamma}{\delta \ln a} \qquad (1)$$

indicate that such films as produced by soluble substances are only one molecule in thickness.

Additional evidence for the monomolecular theory is given by the values thus far obtained for the amount of soap adsorbed at the oil-water interface in emulsions. Thus Griffin,[1] van der Meulen and Rieman,[2] and Harkins and Beeman[3] have all obtained values which agree with the theory. The direct method used by them has not, however, attained a very high degree of accuracy.

A different type of direct method devised by Donnan and Barker[4] gives in its latest form results of a different order. Thus McBain and Davies[5] passed bubbles of gas through solutions of amyl alcohol and of paratoluidine in water, collected the films from the bubbles, and found that the excess in the surface corresponds to a bi- or tri-molecular film. Similar work by Harkins and Gans[6] with the much less soluble nonylic acid had, however, indicated a monomolecular film.

By the "direct" bubble method, McBain and Davies obtained an area of 14 sq. Å per molecule adsorbed from the more concentrated solutions of paratoluidine, while Gans and Harkins[7] by the use of Equation (1) calculated the mean molecular area as twice as large, or 28.5 sq. Å. In making this calculation the writers assumed the correctness of the values for the activity of paratoluidine as obtained by McBain, Wynne-Jones and Pollard[8].

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[*] Contribution from Kent Chemical Laboratory of the University of Chicago.

[1] Griffin: J. Am. Chem. Soc., 45, 1648 (1923).

[2] Van der Meulen and Rieman: J. Am. Chem. Soc., 46, 876 (1924).

[3] Harkins and Beeman: Colloid Symposium Monograph, 5, 27 (1927); J. Am. Chem. Soc., 51, 1674 (1929).

[4] Donnan and Barker: Proc. Roy. Soc., 85A, 557 (1911).

[5] McBain and Davies: J. Am. Chem. Soc., 49, 2230 (1927). Since the completion of the work here presented, several papers on this subject by McBain and his coworkers have appeared: Laing, McBain and Harrison: Colloid Symposium Monograph, 6, 63 (1928); McBain and DuBois: J. Am. Chem. Soc., 51, 3534 (1929).

[6] Harkins and Gans: Colloid Symposium Monograph, 5, 40 (1927).

[7] Gans and Harkins: J. Am. Chem. Soc., 52, 2289 (1930).

[8] McBain, Wynne-Jones, and Pollard: Colloid Symposium Monograph, 6, 57 (1928).

However, any inaccuracy in the activities cannot be sufficient to make the two methods agree.

It is evident that the present status of our knowledge of the thickness of such films from soluble substances is altogether unsatisfactory and is confusing even to the expert in this field. Further work is essential to explain the disagreement, and to decide between the following alternatives which may be considered:

1. The adsorption equation is correct and some unknown error is inherent in the "direct" method of McBain and Davies.

2. Neither the adsorption equation nor the direct method gives the true values. Probably then the correct results are intermediate.

3. The method of McBain and Davies gives correct results, and the adsorption equation has not been derived by a correct method.

In this connection it is important to keep in mind what is almost universally forgotten, that the "adsorption" Equation (1) is not Gibbs' equation for adsorption. His equation

$$d\gamma = -SdT - u_1 d\mu_1 - u_2 d\mu_2 \qquad (2)$$

contains the two unknown adsorptions, u_1 and u_2, and thus cannot be solved unless a relation between them can be found. McBain and Davies consider that even Gibbs' equation is incorrect and that it should include an electrical term, as follows:

$$d\gamma = -SdT - u_1 d\mu_1 - u_2 d\mu_2 \quad \ldots \quad -edV \ . \qquad (3)$$

It seems apparent, however, that the electrical term should not be included for an experiment in which thermodynamic equilibrium is attained, and in which there is no difference of applied potential between the liquid and the gas. Thus, if from the thermodynamic standpoint Equation (1) is correctly derived it is correct without the inclusion of the above mentioned electrical term, and if it is incorrectly derived the inclusion of the electrical term will not make it correct.

It is, then, obvious that if the bubbles in the experiments of McBain and Davies are so highly charged that the term $-edV$ becomes large, then their method should not give the adsorption for an ordinary plane surface, and this would mean that the film is polymolecular only when a large potential is applied through the surface. Our opinion is that no such high potential difference at the surface exists, and that the term $-edV$ is in general negligible and should not be included.

Since the results of McBain and Davies were not in accord with our results in which the less soluble nonylic acid was used, it seemed advisable to repeat their work on amyl alcohol and paratoluidine in order to determine the effect of other variables, such as the size of the bubbles. The apparatus was similar to that used earlier in this laboratory[6] except that the form of collecting tube for the films was that used by McBain and Davies.

2. Apparatus and Procedure

The apparatus employed for the direct determination of adsorption in the air-solution interface is shown in Fig. 1, which is drawn to scale. The liquids in the various parts of the diagram are all samples of the same aqueous solution of the substance under investigation. The uniform bubbles in the regular stream pictured in the adsorption tube 34 pass along this tube to the point 37, where they rise in the inverted U-tube, while the solution around them drains downward. These bubbles which contain in their surfaces the solute adsorbed in their passage through the adsorption tube 34, travel single-file around the U-tube, burst, and the resultant liquid drops down into flask 39. The solution which collects in this flask is therefore more concentrated (with organic solutes) than that in tube 34. The air within the bubbles passes on through the wet-test meter 53.

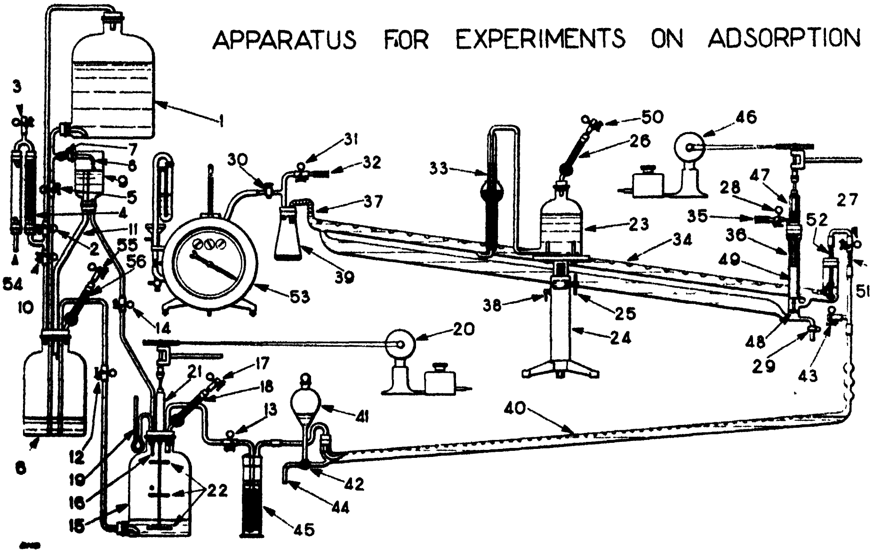

Fig. 1

If the collection of the films is to be kept efficient, the level of the solution at point 37 must be kept constantly at the proper height. This is accomplished by reservoir 23, which is connected with the adsorption tube 34 through tube 33. When the level has fallen appreciably at point 37, it is brought back to its initial position by reservoir 23, which is raised by means of the rack and pinion 24. The mercury seal 33 permits a change of elevation over a 12 cm. range, while a small quantity of air trapped by the four tubes which form the seal keeps the solution from contact with the mercury.

Adsorption may set up various non-uniformities in concentration within tube 34. Such changes are prevented by the use of the small pump 48, operated by motor 46 through the mercury seal 47. The pump creates a gentle counter-current against the stream of bubbles in tube 34 and mixes the solution in this tube with that in the larger tube just beneath. A sufficiently uniform concentration is thus maintained. At the left side of the apparatus, the two tubes are sealed together far enough from point 37 to avoid any disturbances in the collection of the films. Tube 34 is inclined to such an extent that each bubble remains within it for a period of several times that required for complete adsorption.

The air which forms the bubbles is completely saturated with respect to the solution before it arrives at the bubble-forming tip 52. This saturation is secured first by fifteen minutes of vigorous stirring of both air and solution in bottle 15, in which the air is under a pressure sufficiently above that of the atmosphere to ensure its passage through the entire apparatus. Then the air goes through the Fisher-Milligan wash-bottle 45, which almost completes the saturation. To make saturation certain, the air finally passes through the saturation tube 40 in bubbles that burst at the top of the tube. This tube contains solution of the same concentration as that in the adsorption tube 34.

The pressure in bottle 15 is maintained at a constant value by means of the unvarying head of solution between bottles 9 and 15. As air leaves bottle 15, solution from bottle 9 enters through tip 16 to take its place.

The procedure followed in each determination will be made clear by a more detailed description of the apparatus. It will be noticed in particular that the solution in tubes 34 and 40 come in contact with nothing but air, glass and gold-plate.

Reservoir 1, which communicates with the atmosphere through soda-lime tube 4, contains about six liters of the solution under investigation. A thin stream of solution enters bottle 9, which is under atmospheric pressure. The level in this bottle is maintained constant by a slight overflow down the sides of the wide tube 11. Some of the solution runs into bottle 15 through tip 16 until the increased pressure in bottle 15 stops the flow. This pressure, which amounts to 5 cm. of mercury above atmospheric, remains constant throughout the experiment. By means of the small motor 20, operating through the mercury seal 21, the air in the bottle is stirred vigorously for fifteen minutes before each experiment, in order to saturate the air with the vapor from the solution.

Both the adsorption tube 34 and the saturation tube 40 are filled with the solution, the latter through bulb 41, and the former through reservoir 23, the contents of which can be drawn over into tube 34 by suction at tube 32, with the necessary clamps closed. The tubes are emptied, the solutions well mixed, and the tubes refilled. This operation is again repeated, until the tubes contain solutions of the same concentration. At this time, wash bottle 45 is well rinsed and filled with solution.

Motor 46 is started, and maintains a slow counter-current of solution down tube 34 during the experiment, as described above. Next a 100 c.c. sample of the contents of the adsorption tube is drawn over into flask 39 and poured into a glass-stoppered flask labelled A.

Clamp 13, heretofore closed, is opened, and air enters bottle 45 and thence tube 40 in a stream of small bubbles. This air, saturated with respect to the solution, emerges from the collapsing bubbles, goes through capillary 51, which is necessary for proper operation, and passes down tube 52, which is of thick-walled glass, flattened and ground at the lower end. Each bubble formed at this tip escapes upward on reaching its proper size, and encounters a gold-plated brass baffle plate, which deflects it forward along tube 34. At this time, reservoir 23 is kept so low that the bubbles burst below point 37, and the liberated air enters a fresh flask 39 and finds its exit through meter 53.

The apparatus is now in working order. The stream of bubbles is stopped by closing clamp 27, the level of the solution is carefully adjusted to point 37, the meter is read, the time noted, and the bubbles started. Upon reaching the outlet at point 37, the bubbles mount in rapid succession, pushing each other along and draining until nothing but a thin envelope is left around each. These films pass around the inverted U-tube, collapse at its end, and drop down into flask 39, while the enclosed air passes on through the meter. During the experiment, the level is maintained at such a point 37 that the collection of films is most efficient. At frequent and regular intervals, the time of formation of a convenient number of bubbles, usually 100, is determined with a stop-watch. The rate of rotation of the pump is also measured, but was found not to affect the results noticeably. The time each bubble takes to traverse the entire length of the adsorption tube is about 15 seconds.

After enough solution for the analyses has been collected in flask 39, the stream of bubbles is stopped, the exact time again noted, stopcock 30 closed, and motor 46 stopped. The liquid in flask 39 is poured into a weighed glass-stoppered container, labelled B, and its weight is later determined. Without delay, flask 39 is replaced and about 100 cc. of the solution closest to the outlet is drawn over. This solution, which contains any adsorbed solute that may have been skimmed off from each bubble in its passage up the inverted U-tube, is placed in a glass-stoppered flask labelled C. The contents of tube 34 are withdrawn through outlet 29, and after a thorough mixing a 200 cc. sample is separated and placed in a glass-stoppered flask labelled D. About 100 cc. of the solution in tube 40 is also set aside in a glass-stoppered flask labelled E. By means of a suction pump attached to tube 54, the solutions distributed in the left-hand half of the apparatus may be drawn back up into reservoir 1.

From the measured rate of formation of the bubbles and the time of duration of the experiment, the number of bubbles formed is calculated. Since the total volume of air passed is recorded by the meter, the volume of each bubble is easily determined. Measurements of the shapes of bubbles of different volumes permit the calculation of the surface area of each bubble, and hence of the entire area exposed for adsorption. The analyses of the five samples of solution taken give data for the calculation of the total number of adsorbed molecules of solute carried over into flask 39 by the known adsorbing area. Thus is found the molecules of solute adsorbed on each square centimeter of surface and, reciprocally, the apparent surface area occupied by each adsorbed molecule in the surface region. The calculation of the adsorption will be discussed in detail below.

Determinations of the adsorption were made for various concentrations of *iso*amyl alcohol solutions for bubbles of one size, and for both *iso*amyl alcohol and *p*-toluidine solutions, for different sizes of bubbles but for only one concentration, suitably chosen for each solute. Four or five experiments were carried out for each concentration as well as for each size of bubbles. After every two or three experiments, the adsorption tube 34 and the saturation tube 40 were cleaned with hot dichromate cleaning solution and very thoroughly rinsed with distilled water. The inverted U-tube outlet was cleaned with particular care, as it was essential for proper collection of films that the solution should wet the glass at the outlet, as was observed also by McBain and Davies. Greater difficulties were met in this respect with the *p*-toluidine solutions than with those of *iso*amyl alcohol. In a clean outlet tube, however, the former substance gave less trouble, since the films of *p*-toluidine solutions were more stable than those of *iso*amyl alcohol solutions. Whenever the concentration of solution or the solute employed was changed, the entire apparatus was cleaned.

3. Analysis of Solutions

All solutions were analyzed in a Zeiss interferometer, equipped with both a 2 cm. and an 8 cm. cell. To obtain the accuracy necessary for this work, the interferometer was housed in a heat-insulated copper container supplied by a pump with water from an adjacent thermostat regulated at 25.0°C. The glass-stoppered flasks containing the solution to be analyzed were suspended for an hour in the copper container after which time the cell and the solutions were at the same temperature. The cell was filled directly from the flasks. This procedure made possible rapid and very accurate analyses.

After each analysis, the contents of the cell were removed by means of a rubber-tipped glass tube, attached to a suction pump. Since air sucked through the cell in this operation changed the concentration of the last few drops of solution adhering to the cell walls, these were thoroughly dried before the next analysis with a tightly rolled rod of filter paper.

The readings of the drum of the interferometer were calibrated with respect to each of the solutions used. The readings were determined for a series of solutions of each substance, compared against distilled water as the standard. The 2 cm. cell was used for this purpose. In Fig. 2 the calibration curves are given. By corrected reading is meant the reading of the drum when the solution is compared with distilled water, less the zero reading, when both sides of the cell are filled with water. The double curve for the more concentrated solutions arises from a gradual change in the color fringes in the interferometer spectrum, a change which ultimately shifts the apparently correct setting of the drum by the width of one entire order of the spectrum. This phenomenon is amply discussed in the literature.[9]

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[9] Adams: J. Am. Chem. Soc., **37**, 1181 (1915;) Macy: *ibid.*, **49**, 3070 (1927). A paper by Bartell and Sloan: *ibid.*, **51**, 1637 (1929), which appeared since the completion of the present work, describes the use of an interferometer to measure changes in concentration produced by adsorption.

Each analysis was the average of five settings of the drum. In all cases, duplicate analyses were made. With rare exceptions, these checked each other to well within 0.5 of the smallest drum division. The stock solutions were analyzed in the 2 cm. cell. In order to obtain a much higher accuracy, the 8 cm. cell was employed to measure the concentrations of the five samples of solution, A to E, taken during each experiment, and, for these, a differential method was used, that is, the concentration of each was determined, not with water, but with solution D as the standard. It was shown that, for the same solution, the corrected reading for the 8 cm. cell was, within experimental error, 4.00 times that for the 2 cm. cell.

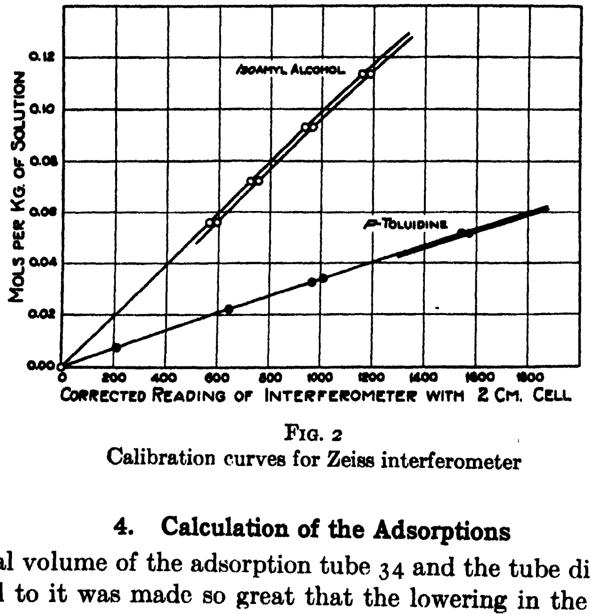

Fig. 2

Calibration curves for Zeiss interferometer

4. Calculation of the Adsorptions

The total volume of the adsorption tube 34 and the tube directly beneath and parallel to it was made so great that the lowering in the concentration of its contents arising from removal of solute by the films was just appreciable. The increase in concentration of solution B, consisting of the collapsed bubble films, was calculated with respect to the average concentration of the solution in the adsorption tube 34 during the experiment, that is, the average of the concentrations of solution A and solution D. This increase in concentration of solution B was corrected by the concentration of solution C relative to solutions A and D. Solution C, which may contain any of the adsorbed solute that may have been removed from the bubbles in their ascent up the right-hand part of the inverted U-tube, was in general found to be somewhat more concentrated than solution D, the final stock solution, and at times more concentrated also than solution A, the initial stock solution. Just what correction to apply on the basis of these differences depends upon the interpretation given of the phenomena occurring within tube 34 during the experiments. To study these, experiments with dyes were performed. A few drops of an aqueous solution of an intensely red dye were injected into various parts of the adsorption tube in order to study the pumping action. On the basis of these experiments, it was decided that, if the collection of the films were perfect, the concentration of solution C would be closely that of the final stock solution D. The following equation was therefore employed to calculate the corrected increase in concentrations due to the films:

$$\Delta R = \left\{(B) - \frac{(A) + (D)}{2}\right\} + \left\{(C) - (D)\right\} \frac{100}{W_B} \qquad (4)$$

in which the symbol (B), for example, represents the concentration of solution B in the arbitrary scale divisions of the interferometer drum, while W_B is the weight of liquid collected from the bubbles, and 100 is the weight in grams of solution C. The quantity in the first brackets represents the increase in concentration found in the collapsed films, while the term which includes the second brackets corrects this increase for any skimming of the films as they mount up the outlet. Since the equation involves only differences of concentration, any arbitrarily selected concentration may be chosen as the zero. For convenience, (D) is chosen as zero, so that (A), (B), and (C) are simply the corrected drum readings relative to (D) as standard of comparison. ΔR is, then, the increase in concentration of solution B, expressed in the arbitrary drum divisions when the 8 cm. cell is used, calculated for the average concentration of the stock solution, and corrected for conditions under which the collection of films would be perfect.

McBain and Davies employed what would correspond to (C) − (A) instead of (C) − (D) in Equation (4) in calculating their results. In the one experiment which they list with sufficient detail to permit a recalculation of their results a difference of 19 per cent is introduced by the difference in the two methods of calculation. While the actual conditions in the tube fall between those assumed in our method of calculation and in that of McBain and Davies, we believe our equation gives much the better approximation to the truth. However, since (D) and (A) never differ greatly *in our experiments* since the adsorption tube has a total volume of two liters—in fact, since they only infrequently differed by more than the experimental error inherent in the interferometer—it is not surprising that the two methods of calculation yield the same average results for most of *our own* experiments.

The concentration of solution E was determined in order to demonstrate, which it did very satisfactorily, that the air, even before entering tube 40, was already saturated with the vapors from the solution.

The wet test meter, graduated in thousandths of a cubic foot, was calibrated and found to read an average of 2.1% too high. From the corrected volume of air that passed through the meter, there was subtracted the volume of solution B, collected in flask 39, since this solution displaced from the flask an equal volume of air which obviously did not originate from collapsed bubbles.[10] The volume thus obtained was the volume of the bubbles themselves.

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[10] McBain and Davies do not seem to have applied this correction.

The surface area of each bubble could not be taken as that of a sphere of equal volume, for the bubbles were obviously not spherical. The bubbles, when in the inverted U-tube, take the form of cylinders, in which form McBain and Davies calculated their areas. But the bubbles assume this shape only in the last two seconds or so of their life. The shape attributed by us to the adsorbing surfaces is that which they possess some few centimeters before they strike the collecting end of the adsorption tube. The largest bubbles were to some extent blunted by their forward motion while the smallest retained an approximately spherical shape. The radius of the adsorption tube 34 was 1.2 cm. Under such an arch, the bubbles took on a form nearly that of an oblate spheroid. As close an estimate of the true surface area of the bubbles as was possible under the circumstances was made by calculating the area of each bubble as that of an ellipsoid of equal volume. The eccentricity of such ellipsoids of various sizes was determined in a series of solutions by trapping the bubbles under an inverted vessel of optically plane glass and measuring their major and minor axes with a travelling microscope and a cathetometer, respectively. The measurements are summarized in Fig. 3. Interpolation between the curves was resorted to for concentrations different from those plotted.

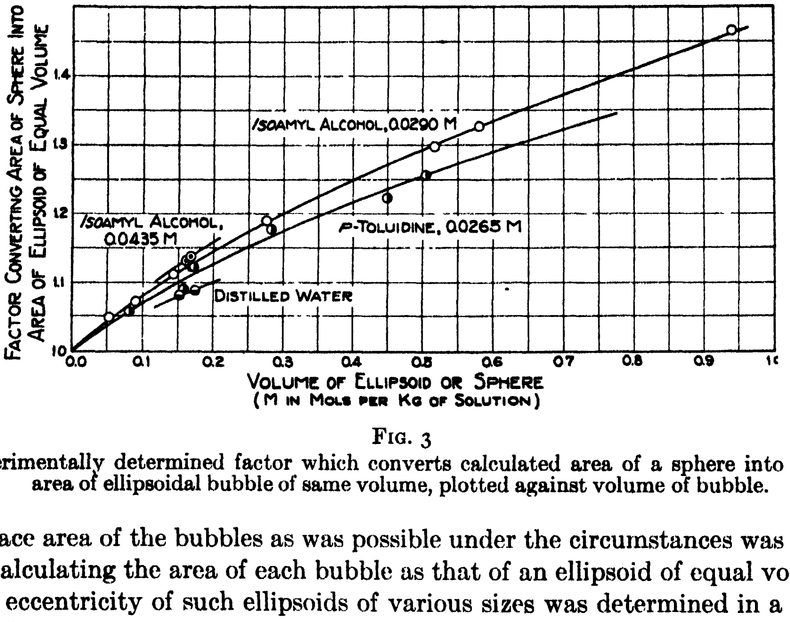

Fig. 3

Experimentally determined factor which converts calculated area of a sphere into actual area of ellipsoidal bubble of same volume, plotted against volume of bubble.

The equation used in the calculation of the adsorption may now be derived. The total number of bubbles, N is,

$$N = \frac{100}{b} 60.0\, t$$

where b is the observed time in seconds required for the formation of 100 bubbles and t is the observed duration of the experiment in minutes. The total volume of the bubbles, V, is

$$V = 27.75\, M - W_B$$

where M is the recorded change in meter reading in thousandths of a cubic foot, 27.75 is the factor correcting this reading by the requisite 2 per cent and at the same time converting the volume into cubic centimeters, and W_B is the weight determined and, closely enough, the volume of the bubble films collected as solution B. The volume of each bubble, v, then is

$$v = V/N$$

and the area, s, of each as an oblate spheroid, is

$$s = 4.836\ v^{2/3}\ F$$

where $4.836\ v^{2/3}$ is the area of a sphere of volume v, while F is the factor, taken from Fig. 3, which converts this area into that of the proper ellipsoid of the same volume. The entire surface area exposed for adsorption is, then,

$$S = Ns.$$

The stock solution, which gives a corrected reading of R divisions against water as a standard, with the 2 cm. cell, corresponds to one containing m moles of solute per kilogram of solution, as determined from Fig. 2. The same solution, but in the 8 cm. cell, would give a corrected reading of 4.00 R divisions. The total number of mols of adsorbed solute which is carried over into solution B by the films is, then,

$$U = \frac{\Delta R}{4.00\ R} \cdot m \cdot \frac{W_B}{1000}$$

where $\Delta R/4.00$ R is the fractional increase in the concentration of solution B.

The adsorption u, in mols per square centimeter of surface, is

$$u = U/S$$

or, expressed in terms of the quantities directly measured,

$$u = \frac{0.01707\ m\ \Delta R\ W_B\ t^{2/3}}{RF\ \{b\ (27.75\ M\ -\ W_B)\}^{2/3}}.$$

When multiplied by Avogadro's number, u becomes u′, the adsorption in molecules per square centimeter of surface. The reciprocal of u′ is a, the mean surface area per adsorbed molecule in the surface region. In the calculation of this mean area, no assumption as to whether the film is polymolecular or monomolecular is involved.

5. Adsorption of Isoamylalcohol and Paratoluidine

Experiments were performed with *iso*amyl alcohol to determine the variation of the adsorption with the concentration of the solution for one size of bubble. For both *iso*amyl alcohol and *p*-toluidine, experiments were carried out to study the dependence of the adsorption upon the size of the adsorbing bubble. The size of the bubble was varied by changing the external diameter of the ground glass tip under which the bubble formation occurred. For each size of bubble, a different inverted U-tube was sealed onto the adsorption tube at point 37. The external diameter of the tip, the internal diameter of the U-tube, and R, the corrected reading in drum divisions given by each solution against water as the standard in the 2 cm. cell are listed in Table I. The concentration m in mols per kilogram of solution, and the corresponding concentration in mols per kilogram of water, as well as the life of the bubbles, are also tabulated. Four to five experiments conducted with portions of the same solution comprise each series. Series A to G are for *iso*amyl alcohol, while series L and M are for *p*-toluidine.

The experiments themselves are listed in Tables II, III, and IV. In these, T signifies room temperature in degrees Centigrade. All of the other symbols have been explained in the derivation of Equation (4). ΔR is calculated by means of Equation (4). Table II shows the variation of the adsorption with the concentration of the solution of *iso*amyl alcohol, for what is closely enough a uniform average size of bubble. Table III contains the data

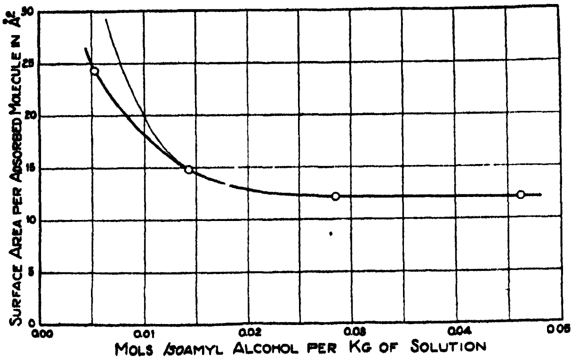

Fig. 4

Variation of molecular area with concentration of solution.

Table I

Series of Expts.	R	m	Mols per Kg. Water	External Diam. of Bubble Forming Tip in Cm.	Internal Diam of Bubble Collecting Tube in Cm.	Life of Bubbles in Secs.
A	53.3	0.0054	0.0054	0.90	0.65	15
B	140.9	0.0143	0.0143	0.90	0.65	15
C	282.3	0.0284	0.0285	0.90	0.65	15–18
D	457.5	0.0460	0.0462	0.90	0.65	13–15
E	290.9	0.0293	0.0294	0.90	0.56	16–18
F	292.1	0.0286	0.0287	0.60	0.43	18–20
G	300.7	0.0303	0.0304	1.88	0.90	11–12
L	781.2	0.0265	0.0266	0.90	0.57	15–17
M	756.1	0.0258	0.0259	1.88	0.90	11–13

A-G Solutions of Isoamyl Alcohol
L-M Solutions of Para-Toluidine

for the variation of the adsorption in *iso*amyl alcohol solutions with the size of the adsorbing bubble. The different concentrations, given in Table I under the same series letter, are very nearly identical, and were so chosen as to fall in the horizontal portion of the curve in Fig. 4, in which region the adsorption does not vary with change in concentration. In Table IV are collected data similar to those in Table III, but for solutions of *p*-toluidine, chosen in the region of concentrations in which, according to the work of McBain and Davies, the adsorption is at its maximum, unvarying value. In all of the derived columns in these tables, the calculations were initially carried out to one more place than is shown. The data in Table II are plotted in Fig. 4 as the heavy full line; the data of Tables III and IV, in Fig. 5 as the heavy full line. The lighter lines in these graphs represent the same data when calculated by the method of McBain and Davies. On account of the minuteness of the quantities measured, the sudden upward jump for the smallest size of bubble taken by the curve in Fig. 5 may be somewhat exaggerated.

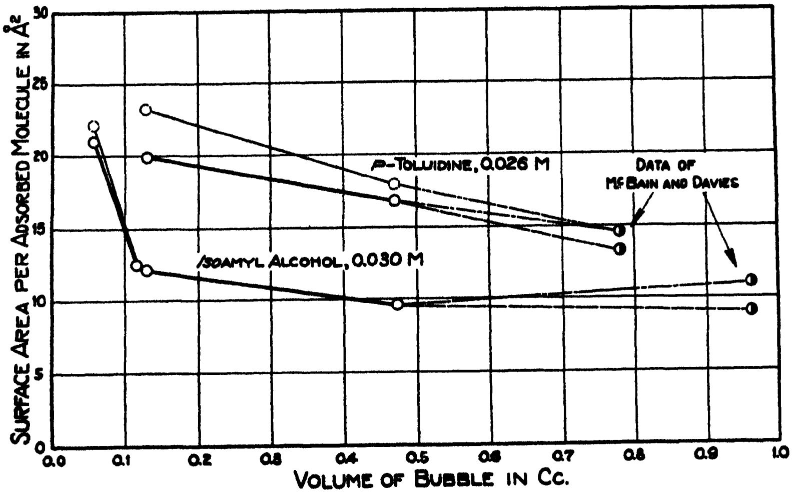

FIG. 5

Variation of molecular area with volume of bubble. Heavy full lines represent results calculated by method given in this paper; light full lines, by method of McBain and Davies. The four points on extreme right of figure represent data obtained by McBain and Davies.

The data of McBain and Davies for those two solutions which fall closest in concentration to the solutions here investigated are also included in Fig. 5. The lower point of each pair is the value as given by McBain and Davies, while the upper point in each case is the average value secured by a recalculation of their data, in which the bubble surfaces are considered as those of oblate spheroids, and not those of cylinders, the form accorded them by these investigators. Their data, if calculated by Equation (4), would probably fall between each pair of values in Fig. 5, so that their values on the whole agree very well with those now presented.

Table II

Adsorption of Isoamyl Alcohol at Various Concentrations

Series of Expts.	No.	T	t	b	N	M	W_B	v	F
A	1	26	15.0	30.7	2930	16.6	42.8	0.1425	1.082
A	2	28	15.0	26.6	3385	19.0	50.0	0.1410	1.081
A	3	28	15.0	35.0	2570	14.7	42.8	0.1420	1.082
A	4	28	15.0	28.5	3160	17.3	65.5	0.1330	1.074
							Average	0.1395	
B	1	28	15.0	29.6	3040	16.4	62.8	0.1290	1.081
B	2	28	15.0	32.7	2750	14.9	54.4	0.1305	1.082
B	3	27	15.0	24.2	3720	20.0	55.5	0.1345	1.085
B	4	27	15.0	23.0	3915	22.1	74.1	0.1380	1.087
							Average	0.1330	
C	1	27	15.0	36.4	2475	12.2	53.3	0.1155	1.088
C	2	26	15.0	34.5	2610	14.0	43.3	0.1325	1.100
C	3	26	15.0	34.6	2600	14.0	48.7	0.1305	1.099
C	4	26	15.0	35.0	2570	14.0	49.3	0.1320	1.100
C	5	26	15.0	37.2	2420	13.9	52.8	0.1380	1.103
							Average	0.1295	
D	1	24	20.0	28.0	4285	22.5	57.0	0.1325	1.116
D	2	23	20.0	26.0	4615	25.0	72.6	0.1345	1.118
D	3	28	15.0	22.7	3965	20.4	54.4	0.1290	1.114
D	4	28	15.0	21.3	4225	22.7	62.8	0.1340	1.118
D	5	28	15.0	21.6	4165	21.7	60.7	0.1300	1.114
							Average	0.1320	

Series of Expts.	No.	S	(A)	(B)	(C)	ΔR	u $\times 10^{10}$	u′ $\times 10^{-14}$	a in Å²
A	1	4185	0.3	2.6	0.0	2.5	6.5	3.9	25.4
A	2	4795	0.4	2.6	−0.1	2.2	5.8	3.5	28.4
A	3	3665	0.2	2.5	0.0	2.4	7.1	4.3	23.2
A	4	4235	0.6	2.4	0.0	2.1	8.2	5.0	20.1
								Average	24.3
B	1	4060	0.1	3.2	0.2	3.5	13.7	8.3	12.0
B	2	3705	0.0	2.7	0.2	3.1	11.5	7.0	14.3
B	3	5120	0.0	3.7	−0.1	3.5	9.7	5.9	17.1
B	4	5490	0.0	3.1	0.0	3.1	10.6	6.4	15.6
								Average	14.8
C	1	3085	0.2	2.1	0.9	3.7	16.1	9.7	10.3
C	2	3605	−0.1	2.9	0.4	3.9	11.8	7.1	14.0
C	3	3560	−0.1	3.1	0.4	4.0	13.8	8.3	12.0
C	4	3545	0.0	3.0	0.5	4.0	14.0	8.5	11.8
C	5	3440	0.0	2.7	0.4	3.5	13.5	8.2	12.2
								Average	12.1
D	1	6010	0.1	5.8	−0.1	5.6	13.4	8.1	12.4
D	2	6555	1.0	5.1	0.3	5.0	13.9	8.4	11.9
D	3	5455	−1.3	5.1	0.0	5.8	14.5	8.8	11.4
D	4	5990	−0.2	4.1	0.3	4.7	12.4	7.5	13.3
D	5	5760	0.4	4.5	0.8	5.6	14.8	9.0	11.1
								Average	12.0

TABLE III
Adsorption of Isoamyl Alcohol for Various Sizes of Bubbles

Series of Expts.	No.	T	t	b	N	M	W_B	v	F
C	1	27	15.0	36.4	2475	12.2	53.3	0.1155	1.088
C	2	26	15.0	34.5	2610	14.0	43.3	0.1325	1.100
C	3	26	15.0	34.6	2600	14.0	48.7	0.1305	1.099
C	4	26	15.0	35.0	2570	14.0	49.3	0.1320	1.100
C	5	26	15.0	37.2	2420	13.9	52.8	0.1380	1.103
							Average	0.1295	
E	1	25	45.0	42.7	6325	26.5	48.7	0.1085	1.083
E	2	27	45.0	59.5	4540	19.4	50.0	0.1075	1.082
E	3	28	40.0	32.5	7385	35.2	52.0	0.1250	1.093
E	4	29	41.0	40.4	6090	25.6	55.5	0.1075	1.082
E	5	28	35.0	32.7	6420	32.6	65.8	0.1305	1.099
							Average	0.1160	
F	1	28	90.0	60.8	8880	19.8	42.5	0.0570	1.049
F	2	27	90.0	52.8	10225	24.3	53.6	0.0605	1.052
F	3	26	90.0	51.2	10545	23.2	44.6	0.0570	1.049
F	4	26	105.0	52.4	12025	26.4	52.9	0.0565	1.049
F	5	26	90.0	48.0	11250	24.2	44.7	0.0555	1.048
							Average	0.0575	
G	1	25	25.0	68.0	2205	36.0	57.0	0.4270	1.258
G	2	28	15.0	42.0	2140	37.3	76.9	0.4470	1.269
G	3	27	20.0	53.6	2240	40.2	71.1	0.4665	1.276
G	4	27	20.0	60.0	2000	37.8	81.2	0.4840	1.282
G	5	27	15.0	54.0	1665	34.9	66.5	0.5410	1.307
							Average	0.4730	

Series of Expts.	No.	S	(A)	(B)	(C)	ΔR	u $\times 10^{10}$	u′ $\times 10^{-14}$	a in Å²
C	1	3085	0.2	2.1	0.9	3.7	16.1	9.7	10.3
C	2	3605	−0.1	2.9	0.4	3.9	11.8	7.1	14.0
C	3	3560	−0.1	3.1	0.4	4.0	13.8	8.3	12.0
C	4	3545	0.0	3.0	0.5	4.0	14.0	8.5	11.8
C	5	3440	0.0	2.7	0.4	3.5	13.5	8.2	12.2
								Average	12.1
E	1	7540	0.0	8.9	0.2	9.3	15.1	9.2	10.9
E	2	5370	0.0	5.1	0.5	6.1	14.3	8.7	11.5
E	3	9770	0.0	7.4	0.5	8.4	11.3	6.8	14.7
E	4	7205	−0.3	6.7	0.3	7.4	14.4	8.7	11.5
E	5	8790	0.2	5.9	0.3	6.3	11.9	7.2	13.9
								Average	12.5
F	1	6680	0.0	3.3	0.7	5.0	8.0	4.9	20.5
F	2	8035	−0.3	4.5	0.2	5.1	8.6	5.2	19.3
F	3	7915	0.3	4.4	0.5	5.5	7.7	4.7	21.4
F	4	8985	0.0	4.4	0.6	5.5	8.2	5.0	20.2
F	5	8320	0.3	4.0	0.6	5.2	7.1	4.3	23.4
								Average	21.0
G	1	7610	0.1	6.3	1.4	8.8	16.6	10.1	9.9
G	2	7690	−0.4	5.5	0.9	6.9	17.4	10.5	9.5
G	3	8310	−0.2	6.0	1.3	7.9	17.0	10.3	9.7
G	4	7645	−0.2	5.0	1.2	6.5	17.4	10.5	9.5
G	5	6995	−0.3	6.1	0.8	7.5	18.0	10.9	9.2
								Average	9.6

TABLE IV
Adsorption of Para-Toluidine for Various Sizes of Bubbles

Series of Expts.	No.	T	t	b	N	M	W_B	v	F
L	1	25	31.0	48.6	3825	19.7	46.1	0.1310	1.087
L	2	27	40.0	52.2	4600	22.2	59.2	0.1210	1.081
L	3	24	30.0	56.2	3335	18.0	53.6	0.1340	1.089
L	4	24	40.0	45.6	5265	27.7	74.3	0.1320	1.088
L	5	23	45.0	47.0	5745	30.0	71.9	0.1325	1.088
							Average	0.1300	
M	1	24	37.0	60.0	3700	58.0	69.4	0.4155	1.215
M	2	25	30.0	62.0	2905	48.3	59.2	0.4415	1.225
M	3	25	30.0	49.2	3660	61.3	73.9	0.4445	1.229
M	4	25	25.0	58.4	2570	48.8	61.9	0.5035	1.248
M	5	26	30.0	51.6	3490	72.2	81.7	0.5510	1.269
							Average	0.4710	

Series of Expts.	No.	S	(A)	(B)	(C)	ΔR	u $\times 10^{10}$	u′ $\times 10^{-14}$	a in Å^2
L	1	5185	0.7	11.8	0.1	11.6	8.8	5.3	18.9
L	2	5885	1.2	9.3	0.1	8.9	7.6	4.6	21.7
L	3	4590	0.6	7.5	0.4	7.9	7.8	4.7	21.1
L	4	7180	0.3	9.9	0.0	9.7	8.7	5.3	19.0
L	5	7850	1.2	11.7	0.0	11.1	8.8	5.3	18.7
								Average	19.9
M	1	12120	0.8	20.7	0.1	20.4	10.0	6.0	16.6
M	2	9975	0.6	19.9	0.7	20.8	10.5	6.4	15.7
M	3	12670	1.7	20.2	1.4	21.2	10.6	6.4	15.7
M	4	9810	0.4	16.2	0.3	16.5	8.9	5.4	18.6
M	5	14390	0.6	17.5	1.7	19.5	9.4	5.7	17.5
								Average	16.8

Both the experiments reported and those of McBain and Davies show that the adsorption in the gas-solution interface, as measured by the method described, increases with concentration until it reaches a constant value which is much greater than corresponds to a monomolecular film. However, the present experiments indicate that the adsorption decreases with the size of the adsorbing bubble, and may approach, as the bubble is made smaller, the values given by the adsorption equation, correctly used, and by experiments with insoluble films.

Attempts to work with bubbles smaller than those listed were unsuccessful. Even when a uniform stream was secured, the bubbles would stick at the outlet. They seemed too small to mount rapidly enough into the inverted U-tube at the collecting end of the adsorption tube, despite the fact that the vertical distance through which each bubble had to rise was made relatively quite small. When the internal diameter of this collecting tube was made large enough to permit the bubbles to rise with the minimum freedom necessary for any collection of films, the bubbles would not drain properly but would carry over between them enough liquid to start a syphoning of the contents of tube 34 into flask 39. The films arising from the largest size of bubbles drained at point 37 with the least difficulty and seemed in general to carry over less solution per unit area of adsorbing surface than the smaller sizes of bubbles.

The internal diameter of the inverted U-tube in the apparatus of McBain and Davies was 1.30 cm. These workers showed that when their bubbles were so large as to form cylinders over 1.1 cm. in length in this tube, only the front and rear end of each cylinder seemed to move forward, while the sides of the cylinder pressed too firmly against the walls of the tube to be able to move. They found the adsorption to decrease with increase in length of the cylinder, once the bubble exceeded the length of 1.1 cm. This phenomenon was also studied in the present case with an inverted U-tube which was 0.90 cm. in internal diameter. The results are presented in Table V. It appears that bubbles of volume greater than 0.55 cc. formed cylinders in this tube which were incapable of proper motion in the collecting tube. A bubble in the shape of a cylinder 0.90 cm. long and 0.90 cm. in diameter has a volume of 0.57 cc. Hence the observation of the investigators mentioned is corroborated. In the experiments here reported, the diameter of the outlet for each size of bubble was chosen as small as possible for efficient collection of films, but yet so large that the bubbles formed cylinders of diameter exceeding their length.

TABLE V

Variation of Adsorption with Volume of Bubble for One Size of Film-Collecting Outlet

Series of Expts.	No.	N	v	S	u $\times 10^{10}$	u′ $\times 10^{-14}$	$a_\circ$ in Å^2
G	1	2205	0 427	7610	16.6	10.1	9.9
G	2	2140	0.447	7690	17.4	10 5	9 5
G	3	2240	0.467	8310	17.0	10.3	9.7
G	4	2000	0.484	7645	17.4	10 5	9.5
G	5	1665	0.541	6995	18.0	10.9	9.2
G	6	2360	0.579	10495	15 7	9.5	10.5
G	7	2440	0.593	11060	14.6	8.8	11.3
G	8	2220	0.625	10540	13.6	8.3	12.1
G[1]	9	1830	0.728	9900	11.4	6.9	14.5

Blank experiments were performed from time to time to study the operation of the apparatus. The procedure followed in these was the same as in the normal experiments, except that at the beginning of the experiment, just after sample A had been taken, 100 cc. of the contents of the adsorption tube were sucked over into flask 39, while the level of the solution at point 37 was maintained so low during the experiment that no bubble films could get over into the flask. In this way, two effects were studied, for it could now be determined whether the air entering the adsorption tube was saturated with respect to the solution, and, what is very important, whether this air, in passing over the solution in flask 39, affected its concentration. The results indicated that the air passing through the solution in the adsorption tube and over any solution in flask 39 did not change the concentration of either solution appreciably. Hence all concentration changes discovered in the normally conducted experiments were due solely to transportation of solute by adsorption.

6. Purification of Materials

By the use of the surface tension data in Volume V of International Critical Tables several substances were selected which are fairly soluble in water and which lower the surface tension of water markedly. *Iso*amyl alcohol, *p*-toluidine, *p*-cresol, and benzoic acid were chosen. Solutions of these which were 0.8 saturated, 0.4 saturated, and 0.2 saturated were prepared and the stability of the foam produced by each under the same conditions of vigorous shaking was observed. Although *p*-cresol behaved well in the most dilute solution, *iso*amyl alcohol and *p*-toluidine were selected as being more suitable for this type of work. The most stable films were given by *p*-toluidine. These two substances were employed also by McBain and Davies.

The *iso*amyl alcohol was obtained from the Eastman Kodak Co. It was shaken with a saturated aqueous solution of sodium bisulfite, washed well with water, and refluxed for three hours over 3 N sodium hydroxide solution. Then, after thorough washing, first with water and finally with dilute hydrochloric acid, it was twice refluxed over fresh lime for two hour periods and distilled over a third portion of fresh lime. It was redistilled, and the fraction coming over in the interval 130.2°-130.5°C under a pressure of 748 mm. of mercury was used. (International Critical Tables: 130.5°C.). The density of this alcohol, d_4^{20}, was 0.81038, while its surface tension at 20.0°C, determined by the drop-weight method, was 23.73 dynes per cm. It contained 20 per cent of the optically active isomer.

The *p*-toluidine used was the best procurable from the Eastman Kodak Co. It was dissolved in ether, and the solution was washed with water and then dried over anhydrous sodium sulfate. The solution was filtered and dry hydrogen chloride was passed into it. The hydrochloride precipitated was isolated by filtration, washed well with ether, and the *p*-toluidine was liberated with a slight excess of sodium hydroxide solution. The *p*-toluidine was further purified by steam distillation. The snow-white solid obtained was sucked dry on a filter and finally dried *in vacuo* over phosphorus pentoxide for several days. It melted at 43.2°C. (International Critical Tables: 43.7°C.)

All of the solutions were prepared with distilled water. The solutions of *p*-toluidine turned faintly amber after several days standing. However, Experiment L1 was performed one hour after the solution was prepared, and Experiment L2, one hour later, while the solution was still colorless. Experiment L5 was conducted after the solution had aged five days. The results of these experiments demonstrate that the slight coloration observed had no appreciable effect.

7. Conclusion

The direct dynamic method for determining adsorption in the gas-liquid interface yields results for such substances as *p*-toluidine and *iso*amyl alcohol which are definitely greater than those derived from the inexact form of the adsorption equation. In fact, the adsorbed solute cannot lie entirely in a monomolecular film if the results for the larger bubbles are correct, as a comparison of the values listed in Table VI will show. However, the values lead to the conclusion that the adsorption decreases as the size of the adsorbing bubble decreases and may approach the value for each solute which is obtained from experiments with insoluble films.

TABLE VI

Surface Areas of Molecules in Sq. Å

a. Direct Measurement of Adsorption		
Volume of Bubble in cc.	0.13	0.47
Molecular Area for *p*-Toluidine	21	17
Molecular Area for Isoamyl Alcohol	13	10
b. Measurements of Insoluble Films		
Benzene Ring perpendicular to Surface		23.8[1]
Normal Alcohols		21.6[2]

Summary

1. Direct measurements by the bubble method of the adsorption of *p*-toluidine and of *iso*amyl alcohol in the air-solution interface are described.

2. Results in partial agreement with those of McBain and Davies, in that they represent an adsorption in excess of that deduced from the adsorption equation and that predicted by measurements of insoluble films, are obtained. However, the adsorption secured in our measurements is in general smaller than that obtained by McBain and Davies. Differences in the methods of calculation obscure the experimental discrepancy.

3. Evidence is presented which shows that the adsorption appears to decrease as the adsorbing bubbles grow smaller, and may approach the value for each solute which is obtained from the adsorption equation and from experiments with insoluble films.

4. The disagreement between the adsorptions expected and those found is discussed.

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[1] Adam: Proc. Roy. Soc., **103**, 676 (1923).

[2] Adam: Proc. Roy. Soc., **101**, 452 (1922); **106**, 694 (1924).

THE CHEMICAL REACTIVITY OF THE FUSED BASES

I. The Action of the Alkali Amides upon Electropositive Metals[1]

BY W. CONARD FERNELIUS[2] AND F. W. BERGSTROM

In an earlier series of investigations[3] one of us has examined the action of liquid ammonia solutions of the ammono bases, potassium and sodium amides, upon a number of elements. It was found that an electropositive metal, such as magnesium, reacts in the sense of the equation,

$$2NH_3 + Mg + 2KNH_2 = Mg(NHK)_2 \cdot 2NH_3 + H_2$$

to form potassium ammono magnesiate and hydrogen, just as zinc reacts with an aqueous solution of potassium hydroxide to form potassium zincate and hydrogen,

$$Zn + 2KOH = Zn(OK)_2 + H_2$$

Whereas such a reaction in water is fairly rapid, the analogous reaction in liquid ammonia is slow, enabling the observer to gain an idea of the steps involved and the intermediate products. Thus it was found that magnesium first reacts with a liquid ammonia solution of potassium amide to liberate potassium, which is detected by the opaque blue color of its dilute solution and the coppery lustre of the highly concentrated solution,[4] the reaction probably proceeding in accordance with the equation,

$$Mg + 2KNH_2 \rightleftharpoons Mg(NH_2)_2 + 2K.$$

To understand this apparently anomalous displacement of one metal by a less electropositive metal, one has but to recall that dilute solutions of the alkali metals in liquid ammonia are ionic in character,[5] the positive ions being the normal ions of the alkali metal while the negative ions are solvated electrons, e^-. Since potassium amide forms potassium, K^+, and amide, NH_2^-, ions, the reaction of a solution of this substance with magnesium is but a reaction between four ions, K^+, NH_2^-, Mg^{++} and e^-, in accordance with the equation,

$$2K^+ + 2NH_2^- + Mg^{++} + 2e^- \rightleftharpoons Mg(NH_2)_2 + 2K^+ + 2e^-$$

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[1] This paper is a portion of a dissertation submitted to the department of chemistry and the committee on graduate study of Stanford University by Mr. W. C. Fernelius in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented at the Swampscott meeting of the American Chemical Society, September 1928.

[2] Royall Victor Fellow in Chemistry, 1927-8.

[3] Bergstrom: J. Am. Chem. Soc., **45**, 2788 (1923); **46**, 1545 (1924); **47**, 1836 (1925); **48**, 2848 (1926); **50**, 652 (1928); J. Phys. Chem., **30**, 12 (1926).

[4] Although magnesium dissolves slightly in liquid ammonia, the color intensity of the solution is so much less than that of a solution of potassium that there can be no confusing the two. Furthermore, a concentrated solution of potassium has a very coppery luster. Cf. J. Am. Chem. Soc., **45**, 2789 (1923).

[5] Kraus: J. Am. Chem. Soc., **43**, 749 (1921) and previous articles.

Since magnesium amide, $Mg(NH_2)_2$, has a very low solubility in ammonia, it is precipitated and there remains in solution only K^+ and e^- ions, which together constitute a solution of metallic potassium.

The potassium resulting from the equilibrated condition noted above reacts with the solvent to regenerate potassium amide,

$$2K + 2NH_3 = 2KNH_2 + H_2$$

the magnesium serving as a catalyst for this reaction. Furthermore, the amide of the less electropositive metal, being an amphoteric base reacts with the alkali metal amide to form an ammono metallate,[1] in accordance with the equation,

$$Mg(NH_2)_2 + 2KNH_2 = Mg(NHK)_2 \cdot 2NH_3.$$

Purpose of the Investigation

In view of this interesting behavior of the alkali metal amides in liquid ammonia solution it was deemed worth while to extend the study of such reactions to the fused state where the temperature and concentration of the amide would be much greater and where solubility or insolubility in liquid ammonia would not be a factor influencing the course of the reaction. Furthermore, there is at the present time no really satisfactory or comprehensive theory of fusions in the alkali bases and any study pointing toward the formulation of such a theory is valuable. This work was stimulated by an observation of Professor E. C. Franklin that a piece of magnesium ribbon plunged into molten sodium hydroxide has drops of a blue liquid adhering to it upon withdrawal. Such behavior indicates the liberation of metallic sodium in accordance, probably, with the equation,

$$Mg + 2NaOH \rightleftharpoons 2Na + Mg(OH)_2.$$

Historical: The Action of the Amides upon the Elements

Following the discovery of sodium and potassium amides by Gay-Lussac and Thénard, these investigators found that several metals were attacked by potassium amide.[2] Davy, working contemporaneously, studied in a superficial manner the reaction of potassium amide with tellurium and arsenic.[3] Ephraim[4] examined the reactions of sodium amide with sulfur, bromine, iodine and magnesium as well as with a large number of oxides, sulfides, chlorides and ternary salts. Winter[5] observed that an energetic reaction occurred when yellow phosphorus was warmed with sodium amide. Wöhler and Stang-Lund[1] have electrolyzed fused sodium and potassium amides and determined their specific conductivity and decomposition voltages. McGee[2] has also determined the specific conductance of molten sodium amide.[3]

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[1] One will recall that the phenomenon of amphotericity of the basic amides is much more general than the similar property of the basic hydroxides. Not only is there an aluminate, zincate, plumbite, stannite and stannate of potassium, but also a cuprite, a cadmiate, a magnesiate, a calciate, a bariate and even a sodiate in the ammonia system. Furthermore these compounds are for the most part definitely crystalline and easily obtained in a pure condition.

[2] Gay-Lussac and Thénard: "Recherches physico-chimiques," 1, 341 (1811).

[3] Davy: Phil. Trans., 1810, 27.

[4] Ephraim: Z. anorg. Chem., 44, 185 (1905).

[5] J. Am. Chem. Soc., 26, 1484 (1904).

Apparatus and Manipulation

In designing an apparatus for studying fusion reactions there were numerous factors which had to be taken into consideration. It can safely be said that no single technique so far employed has been entirely satisfactory in all of its details. The apparatus finally chosen for this investigation is shown in Fig. 1. It was designed so that the amide fusions could be carried out in a current of ammonia in the complete absence of air and moisture. The fusion chamber (DEFG) consists of a pyrex tube (27 mm. diameter by 60 cm. long, with side arms of 12mm. tubing, as shown) wound with number 27 chromel wire to serve as a heating unit[4] and insulated with 85% magnesia pipe covering. A length of three quarter inch monel metal tubing, *S*, is inserted in the

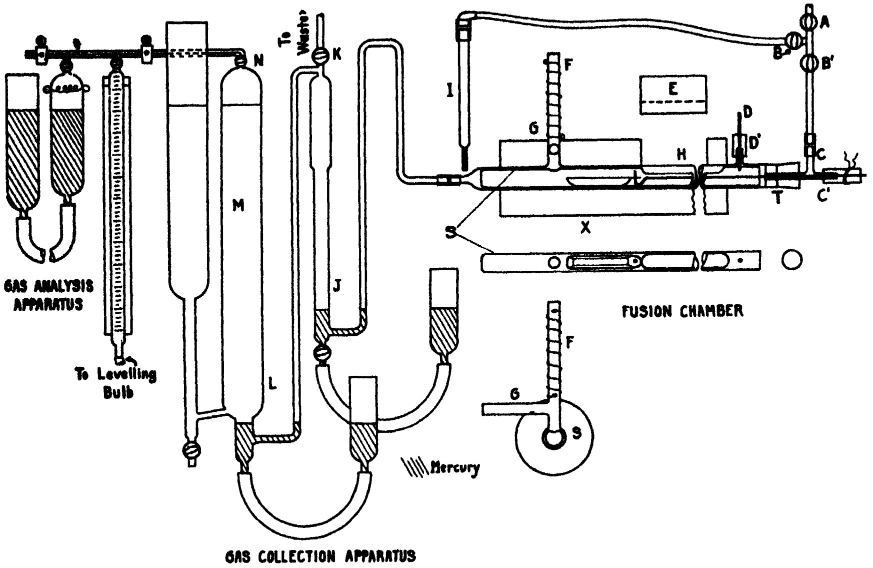

FIG. 1

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[1] Wöhler and Stang-Lund: Z. Elektrochemie, 24, 261 (1918).

[2] McGee: J. Am. Chem. Soc., 43, 586 (1921).

[3] Other important references dealing with the fused alkali amides are Beilstein and Geuther: Ann., 108, 88 (1858); Baumert and Landolt: 111, 1 (1859); Drechsel: J. prakt. Chem., (2) 16, 201 (1877); Wislicenus: Ber., 25, 2084 (1892); Titherly: J. Chem. Soc., 65, 504 (1894); 71, 469 (1897); De Forcrand: Compt. rend., 121, 66 (1895); Dennis and Browne: J. Am. Chem. Soc., 26, 587 (1904); Ruff and Goerges: Ber., 44, 502 (1911); Miles: Proc. Roy. Soc., Edinburgh, 35, 134 (1915); Kraus and Cuy: J. Am. Chem. Soc., 45, 712 (1923); Guntz and Benoit: Bull., (4) 41, 434 (1927). There exists also a voluminous literature on the use of sodium amide in organic chemistry.

[4] The pyrex tube was wound for the entire length covered by the magnesia insulation—including the section E. These windings are not shown in Fig. 1. The two terminals of the wire were tied to glass knobs fused to the glass at the ends of the insulated portion.

furnace to serve as a sheath to protect the glass from the corrosive amide which is often spattered or spilled from the fusion boat, *X*, during the course of a reaction. The upper part of the monel tube on the right was milled away to a depth of about one third its diameter and over about half of its length, to enable the observer to view the molten amide in the boat. Likewise, there is a hole in the metal directly underneath the glass tube *F* through which materials are introduced into the fusion boat. A short length of one eighth inch monel rod, inserted through the tight rubber sleeve, D′, and through a small hole drilled in the metal sheath served to keep the sheath in position. A long monel rod H (1/8 inch in diameter) hooked at one end and working through the rubber sleeve C′ is used to place the fusion boat, a nickel combustion boat 13x75 mm. in size, at any desired position within the fusion chamber. The space E of the insulation is arranged so that it may be removed to enable one to view the interior of the chamber. A resistance heating unit is wound on F, and the side tube G, sealed to F, may also be used for the introduction of materials into the furnace. J is a mercury bubbler which gives a visual measure of the amount of gas passing through the apparatus. The large tube M is filled with dilute air-free sulfuric acid and serves both as an ammonia scrubber and as a gas collector. The apparatus for gas analysis is connected through a capillary with the top of the gas collector, M.

The technique employed when using this apparatus is perhaps best described by giving the log of a typical run. After thoroughly cleaning and drying both the chamber and the sheath, the latter is inserted in the furnace and locked in position. The boat, previously cleaned inside and outside with emery cloth[1] is attached to the manipulative rod, H, placed in the chamber and then moved directly beneath the vertical filling tube, F. All stoppers are now fitted into position and the inlet tube C connected to the pure ammonia line,[2] A-B′, and a slow stream of ammonia admitted to sweep out foreign gases within the system. Stopcock K is open during this time so that all gases are vented to the waste. The heating current for the main furnace is now turned on.[3] The ammonia stream is continued for twenty minutes and during this time the stoppers F and G are removed for a sufficient length of time to insure the removal of all air that may be in these tubes.

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[1] Neither fused amides themselves nor the products of their reaction with the strongly electropositive elements attack or discolor the nickel boats to any noticeable extent. The reaction products of the more electronegative elements, however, exhibit a definite corrosive action upon the nickel. Particularly is this true of tin, lead, arsenic and antimony fusions which leave a rather tightly adherent film of brown-black material clinging to the boat. Phosphorus and the elements of the sulphur group give reaction products which discolor the nickel to a considerable extent, but do not appear to attack it seriously.

[2] The ammonia used is the commercial anhydrous product dried over sodium according to the method of Franklin and Kraus: Am. Chem. J., 23, 285 (1900).

[3] The amount of current passing through the furnace is regulated by means of a lamp resistance. The maximum temperature attained by the furnace is a function of the heating current. Having determined therefore the relation between the maximum temperature and the heating current once and for all, it was possible to dispense with temperature measuring instruments during the course of an experiment. This allowed the use of a smaller furnace.

The alkali metal can now be introduced into the fusion boat. For this purpose an injector tube, I, was prepared by sealing a fine capillary to a wider tube which snugly fits the interior of F. Freshly cut alkali metal a little in excess of the quantity it was desired to introduce into the boat (about a gram) is placed in the injector tube and this latter is connected by means of a rubber tube to the pure ammonia line at B. By closing B′ and opening B air in I was displaced with ammonia. After this was accomplished, ammonia was again directed through the furnace by closing B and opening B′. The tube I was placed inside of F with the end of the capillary about on a level with the top of the boat, and a current passed through the externally wound resistance to melt the alkali metal. After the metal was molten, I was tapped a few times to disengage the melt from the oxide crust. Then, by closing B′ and slowly opening B, the pure molten metal was forced by ammonia pressure through the capillary into the fusion boat, leaving the oxide behind. The injector was then weighed with rubber caps over both ends. Subtracting this weight from the weight of the same when it contained the alkali metal gave the weight of the metal in the boat.

This process completed, the vertical heating unit is shut off, the injector removed and F once more tightly stoppered. The boat is now withdrawn to the fusion space—that portion of the chamber between F and the removable cover, E. This region is the hottest and also the only one where there is absolutely no danger of any spattered material reaching the glass walls. Here the metal is quickly converted to the amide—usually within a half hour. A clear light yellow melt is sufficient indication that the reaction is complete, although, when gases are being collected it is better to run the exit ammonia stream through the acid tower for a time to see that no acid insoluble gases are present in the line. If the reaction that is to be carried out is very vigorous, or if it is desired to collect the gases given off during the reaction quantitatively the amide is allowed to cool, the boat moved under F and the reacting substance added through F or G, the entrance of air into the tube of course being prevented by the current of ammonia passing through F or G into the atmosphere. Then, with F and G tightly stoppered, the boat is withdrawn into the fusion space, stopcock K closed, and the furnace heated to the desired temperature. If a quantitative collection of the gases given off during the reaction is not desired, the solid reactant is added directly to the molten amide in a similar fashion.

Following the completion of the fusion the boat is withdrawn to the cooler part of the furnace—that portion outside of the insulation—and permitted to solidify. Unless otherwise specified, all reactions were carried out at 375°-400°.

The nickel boat containing the cooled melt was now sealed in an ammonia reaction tube according to the methods previously developed by Franklin and co-workers[1] and the products there washed with liquid ammonia and prepared for analysis. In those cases where all of a solid element does not react with the amide, the difference in density of the element and the insoluble reaction product is usually sufficiently great to enable one to carry the precipitate in suspension to the opposite leg of the reaction tube without carrying over any of the unreacted element. In order to transfer the boats to the ammonia tube, a "conveyor", made by sealing a stopcock on the closed end of a wide test tube, was slipped over the end of the pyrex furnace tube, after removal of the stopper, T. Then, with a current of ammonia passing through the conveyor, the end of the furnace was lowered to allow the boat to slide from the furnace into the conveyor, which was at once tightly stoppered. Ammonia pressure to the extent of about twenty centimeters of mercury was allowed to build up within the tube before the stopcock was closed. No apparent harm results if the fusion products be preserved for several days in such containers.

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[1] Franklin: J. Am. Chem. Soc., 27, 831 (1905); 29, 1275 (1907); 35, 1460 (1913); J. Phys. Chem., 15, 510 (1911); 16, 694 (1912); Fitzgerald: J. Am. Chem. Soc., 29, 1694 (1907); Bohart: J. Phys. Chem., 19, 539 (1915).

The technique just described for conducting amide fusions and treating the reaction products has several distinct merits: (1) chemically pure amides are used; (2) the temperature of the fusion chamber can be regulated at will by varying the amount of current passing through the heating unit; (3) any gases other than ammonia evolved during the reactions are quantitatively collected; (4) the melt can be examined optically at any time and the color changes, formation of precipitates, intensity of reaction, etc. determined; (5) the atmosphere in which the fusion is carried out can be changed at will; (6) at no time does the melt come in contact with glass or air and suffer contamination and (7) the use of liquid ammonia, the parent solvent of these nitrogen compounds, to extract the melt does not destroy the reaction products as does water. The disadvantages of the apparatus are (1) the small size of the boats employed prevents one from obtaining any but the smallest amounts of reaction products; (2) the spattering of the melt during some reactions clouds the window after a time, and (3) long time fusions in such an apparatus are inconvenient and wasteful of ammonia.[1] Furthermore, the slow decomposition of the fused amides into their elements introduces a somewhat uncertain blank correction into the analyses of gases evolved during the fusion process. Since the decomposition of the amides produces an alkali metal which reacts with the ammonia atmosphere in the furnace to form an amide and hydrogen, the net reaction should amount to a decomposition of the ammonia into three volumes of hydrogen and one of nitrogen. The heated metal of the sheath may also decompose some ammonia catalytically into its elements. In blank runs the ratio of hydrogen to nitrogen approximated the theoretical value of 3 to 1.

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[1] The second objection is removed by enlarging the furnace sufficiently to allow a thin pyrex tube to be placed around the milled portion of the monel sheath. This tube can be readily replaced when it becomes clouded. It was found convenient also to move the filling tubes, *F* and *G*, to the edge of the uninsulated portion, *E*. This permitted one to see the fusion at the moment the solid reactant was introduced.

Discussion

In general it can be said that the reactions of the fused alkali amides resemble very closely their reactions in liquid ammonia solution. In some cases, however, there are very interesting differences. The reaction of magnesium with fused potassium amide will serve as an admirable example of the reaction of an electropositive metal with a fused alkali amide. Immediately upon adding magnesium to fused potassium amide, the melt becomes blue[1] and globules of potassium form and float about on the surface of the melt. A white precipitate, visible through the clear melt, and disappearing on subsequent heating indicates the presence of magnesium amide. On continuing the fusion in an atmosphere of ammonia, the potassium is converted into amide and the melt becomes clear. When the potassium amide is dissolved by liquid ammonia, potassium ammono magnesiate, $Mg(NHK)_2 \cdot 2NH_3$, remains behind.[2]

The extent of the displacement of sodium from the molten amide by magnesium was approximated by conducting the reaction in an atmosphere of nitrogen and extracting the cooled melt with liquid ammonia. In order to arrive at a relationship between the liberated sodium and the magnesium entering the reaction, it was necessary to apply a number of relatively large corrections to the actual weight of extracted sodium, so the values in the fifteenth column of Table I (Experimental part) are to be regarded as more or less close approximations. Nevertheless it will be seen that almost two atoms of sodium are liberated for each atom of magnesium entering the reaction.

The only other metals to liberate alkali metal in sufficient quantity to color the melt blue were calcium and aluminum. Calcium does not react as vigorously with fused potassium amide as might be expected. A heavy white precipitate of potassium ammono calciate, $CaNK \cdot 2NH_3$, remains after the excess of potassium amide is washed away with liquid ammonia.

Aluminum in the form of wire is not attacked as vigorously by fused potassium amide as is magnesium. Nevertheless, very small globules of potassium could occasionally be seen darting about the surface of the bluish-green molten amide and the aluminum was slowly converted into a white or gray mass insoluble in the fusion. This precipitate, which remained when the potassium amide was dissolved out with liquid ammonia, did not prove to be definite in composition. It is perhaps best to regard it, provisionally, as consisting of ammonous aluminum nitride which has adsorbed potassium amide, since the known compound resulting from the action of potassium amide on ammonous aluminum nitride,[1] potassium ammono aluminate, is readily soluble in liquid ammonia.[2]

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[1] Practically every investigator who has prepared the amides of the alkali metals by passing ammonia gas over the fused metals has reported the formation of a blue colored solution which loses its color when acted upon by an excess of ammonia. Davy: Phil. Trans., **1809**, 42; Beilstein and Geuther: Ann., **108**, 89 (1858); Baumert and Landolt: **109**, 3 (1859); Titherley: J. Chem. Soc., **65**, 504 (1894); **71**, 469 (1897); Rengade: Compt. rend., **140**, 1184 (1905); Wöhler and Stang-Lund: Z. Elektrochemie, **24**, 261 (1918); Guntz and Benoit: Bull., (4) **41**, 434 (1927). McGee: J. Am. Chem. Soc., **43**, 586 (1921) did not observe this color although the present investigation has repeatedly shown it. From the analogy to the blue colored solutions of the alkali metals in liquid ammonia and the amines, Titherley: J. Chem. Soc., **65**, 510 (1894), argued that this color was due to a solution of the alkali metal in the fused amide and this view appears to be correct.

[2] Ephraim (Z. anorg. Chem., **44**, 185 (1905)) studied the reaction of magnesium with fused sodium amide and concluded that magnesium nitride, sodium, and hydrogen were formed. His experimental technique would not have distinguished between magnesium nitride and potassium ammono magnesiate.

The question of whether or not the ammono magnesiate exists in the anammonous form in the molten amide cannot be settled without further experimentation. It seems possible that the salt exists as $Mg(NHK)_2$, since the evolution of ammonia has been observed upon adding magnesium to fused sodium amide in an atmosphere of nitrogen.

Beryllium is dissolved slowly by fused sodium amide with the production of sodium ammono berylliate, $BeNNa \cdot 2NH_3$, which may be readily extracted from the melt by liquid ammonia. Zinc slowly reacts with fused potassium amide to give potassium ammono zincate, $Zn(NHK)_2 \cdot 2NH_3$, which is sparingly soluble in liquid ammonia. Impure cerium is slightly attacked by fused potassium amide. Finely divided metallic germanium[3] reacts readily with fused potassium amide to liberate hydrogen and form a product insoluble in liquid ammonia which may be either potassium ammono germanate, $NGeNHK$, or potassium ammono germanite, $Ge{=}NK \cdot NH_3$, since the percentage of potassium, nitrogen and germanium in the two compounds is almost identical. The atomic ratio of hydrogen evolved to the germanium added is about 3:1, indicating that the ammonia-insoluble reaction product consists of a mixture of germanate and germanite in the approximate ratio of 1:1, formed in accordance with the equations,[4]

$$Ge + KNH_2 + NH_3 = NGeNHK + 2H_2$$
$$Ge + KNH_2 + NH_3 = Ge{=}NK \cdot NH_3 + H_2.$$

In this connection, it may be recalled that when carbon is fused with sodium amide, either sodium cyanide or sodium cyanamide is formed, according to the conditions.[5]

Fused potassium amide converts mercury into a dilute potassium amalgam. Apparently the mercury itself is not attacked, but merely dissolves the potassium resulting from the very slow decomposition of potassium amide into its elements.[6]

Thorium and manganese are attacked slightly by fused potassium amide over a period of ten hours, but the reaction products were not obtained in amounts sufficient for identification. Copper, cadmium, thallium, titanium, zirconium, tantalum, chromium, nickel, platinum and iridium were not attacked by fused potassium amide. Of these metals, zirconium alone was in the form of a powder.[1] Other metals which have been reported as unattacked by fused potassium amide are iron, silver and gold.[2]

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[1] Bergstrom: J. Phys. Chem., **32**, 436 (1928).

[2] Bergstrom: J. Am. Chem. Soc., **45**, 2788 (1923); **46**, 1548 (1924).

[3] The germanium oxide, from which the germanium was prepared by reduction, was a gift of the New Jersey Zinc Company.

[4] An ammono germanate of the approximate composition, NGeNHK, has been prepared in liquid ammonia by the action of potassium amide upon the product of ammonolysis of germanium tetrabromide. (Bergstrom: unpublished observations.)

[5] Sodium cyanide, a sodium ammono carbonite: Franklin: J. Phys. Chem., **27**, 167 (1923); sodium cyanamide, a sodium ammono carbonate: Franklin: J. Am. Chem. Soc., **44**, 1495 (1922). English patents, 12,219; 21,732 (1894); German patents, 117,623; 124,977; 126,241 (1900); 148,045 (1901). Cf. Zentrallblatt, **75**, I, 411 (1904).

[6] At temperatures much above 400°, the fused alkali amides acquire a pale bluish-green color, because of the presence of free alkali metal in solution. This color does not persist at lower temperatures in an ammonia atmosphere.

Wöhler and Stang-Lund (Z. Elektrochemie, **24**, 261 (1918)) found that mercury has no action upon molten sodium amide.

Sodium Hydroxide Fusions

In order to follow the parallelisms between the fused alkali bases of the water and ammonia systems, a few reactions were carried out in fused sodium hydroxide at a temperature of 400° in the amide-fusion apparatus. Sodium dissolves to a slight extent in fused sodium hydroxide, imparting a blue color to the melt. At first the major portion of the sodium floats on the melt, but with lapse of time the two appear to react and form an insoluble solid. The cooled melt was very hard and reacted vigorously with water to form a small amount of gas. This latter behavior would suggest the formation of sodium hydride.[3]

Magnesium under similar conditions gives a blue color to the solution near the strips of the metal and then dissolves completely within a short time. Le Blanc and co-workers[4] have examined the action of sodium and potassium hydroxide on a number of metals and have formulated the reaction with magnesium as one of the type reactions, thus

$$\begin{aligned} Mg + 2KOH &= Mg(OH)_2 + 2K \\ Mg(OH)_2 &= MgO + H_2O \\ 2H_2O + 2K &= 2KOH + H_2 \end{aligned}$$

Had they written in place of (2) above the following,

$$Mg(OH)_2 + 2KOH = Mg(OK)_2 + 2H_2O$$

which is as strongly supported by the experimental results, then the course of the reactions of the aquo and ammono bases on magnesium is the same.

Calcium reacts with fused sodium hydroxide in an atmosphere of nitrogen to form a blue melt and, with lapse of time, a white precipitate that is insoluble in the fused mixture. Since liquid ammonia fails to extract any soluble metal from the cold fusion, free sodium and calcium must be present in very low concentrations in spite of the bluish-green color of the melt at the completion of the reaction. As hydrogen is formed when the cold fusion is hydrolyzed, a portion, at least, of the calcium appears to have been converted into hydride.

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[1] Platinum is attacked very noticeably over long periods of time. Titherley: J. Chem. Soc., **65**, 505 (1894); Dennis and Browne: J. Am. Chem. Soc., **26**, 590 (1904); McGee: **43**, 590 (1921).

[2] *Silver*, Miles: Proc. Roy. Soc. Edinburgh, **35**, 134 (1915); Ruff and Goerges: Ber., **44**, 502 (1911); Wöhler and Stang-Lund: Z. Elektrochemie, **24**, 263 (1918). *Gold*, Franklin: unpublished observations. *Iron*: Wöhler and Stang-Lund: loc. cit.; Titherley: loc. cit.; De Forcrand: Compt. rend., **121**, 66 (1895); Winter: J. Am. Chem. Soc., **26**, 1486 (1904). Carbon in the iron, however, introduces cyanides into the amide. Szarvasy: J. Chem. Soc., **77**, 606 (1900); Dennis and Browne: loc. cit. p. 589.

[3] Hevesy: Z. Elektrochemie, **15**, 529 (1909), has shown that sodium dissolves in sodium hydroxide to the extent of twenty percent (by weight) at 480°. This high solubility may be due, in part at least, to hydride formation.

[4] Le Blanc and Bergmann: Ber., **42**, 4728, 4743 (1909); Le Blanc and Weyl: **45**, 2300, 2312 (1912).

Aluminum wire does not appear to be attacked at all by fused sodium hydroxide in five hours time.

It seems worthy of mention at this point that the reactions of the fused alkali amides considered in the present paper do not require for their interpretation any assumption of acidic dissociation as has been made for the alkali hydroxides.[1] Rather, it would appear more logical to assume a normal dissociation into alkali metal ions and amide ions, $NaNH_2 \rightleftarrows Na^+ + NH_2^-$.

Experimental

Calcium and Potassium Amide. Preparation 1. A freshly cut piece of calcium (0.2 g.) was added to molten potassium amide and the fusion continued for six and one half hours. The white fusion product, which was disintegrated under liquid ammonia only after long and patient shaking, was thoroughly washed with fresh solvent. One half of 0.5141 g. gave 0.0723 g. nitrogen, while the other half gave 0.1089 g. CaO and 0.1892 g. K_2SO_4. The specimen was dried in a vacuum at 20°.

Preparation 2. was in all essentials a duplicate of the preceding. The specimen taken for analysis weighed 0.5764 g. when dried in a vacuum at 20° and 0.5749 g. when heated in a vacuum at 115°. One half of 0.5749 g. gave 0.0820 g. nitrogen while the other half gave 0.1287 g. CaO and 0.2100 g. K_2SO_4.

	Calc. for $CaNK \cdot 2NH_3$	Found I	Found II
Ca	31.5	30.3	31.9
N	33.1	28.1	28.5
K	30.8	33.0	32.7

The results are in better agreement with a formula, $CaNK \cdot 1.5\ NH_3$.

Beryllium and Sodium Amide. The product of the fusion of metallic beryllium with sodium amide was washed several times with large volumes of liquid ammonia to remove the very soluble sodium ammono berylliate. In this operation some sodium amide was necessarily transferred in solution to the other leg of the reaction tube since its solubility is of the order of a gram a liter at ordinary temperatures. The leg of the reaction tube containing the boat was then opened, cleaned out and resealed with the other leg maintained at −40° in a bath of liquid ammonia.[2] The extracted material was then concentrated to a volume of a few cc. to precipitate the major portion of the sodium amide, and then the clear supernatant liquid was decanted into the clean leg of the reaction tube. The solid left after evaporation of the ammonia from this solution was prepared for analysis in the usual manner. The sodium analysis, as expected, runs a little high. One quarter of 0.7133 grams (dried in vacuum at 20°) gave 0.0856 g. nitrogen. A second quarter gave 0.0850 g. nitrogen while the remaining half gave 0.1062 g. BeO and 0.3474 g. Na_2SO_4.

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[1] Fry and others: J. Am. Chem. Soc., **46**, 2268 (1924); **48**, 958 (1926); **49**, 864 (1927); **50**, 1122, 1138 (1928); **52**, 153 (1930). Cf. Strain: **52**, 1217 (1930).

[2] Franklin: J. Phys. Chem., **15**, 510 (1911).

Calc. for $Be(NH_2)NHNa \cdot NH_3$, Be 11.2, N 52.5, Na 28.8. Found, Be 10.8, N 48.0, Na 31.5.

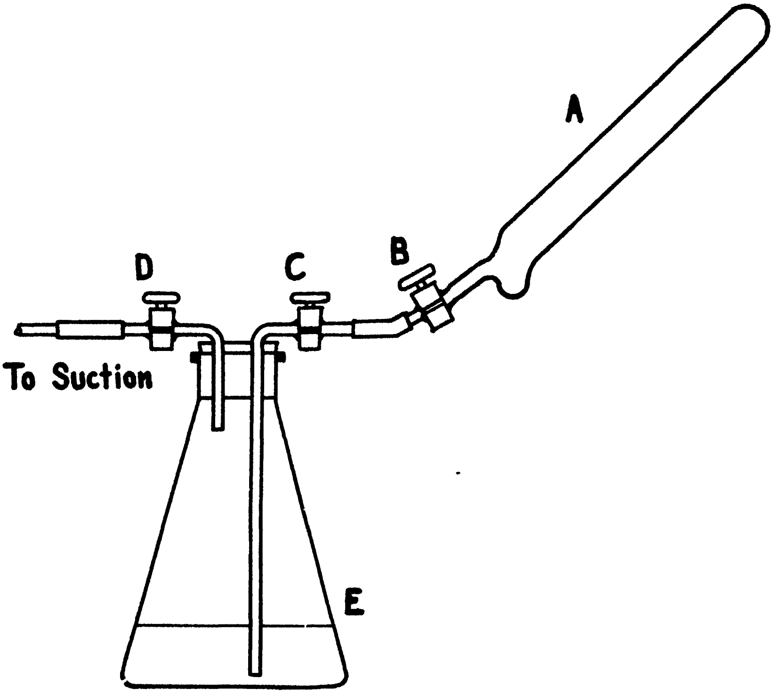

FIG. 2

The Initial Equilibrium between Sodium Amide and Magnesium. A weighed amount of polished magnesium ribbon was added to fused sodium amide in an atmosphere of nitrogen. In the resulting rapid reaction, metallic sodium was formed and floated in the form of a globule on the surface of the melt. The fusion was now quickly cooled and extracted with liquid ammonia until the washings were no longer colored blue—that is, until all of the alkali metal had been washed over. During these washings some sodium was converted to sodium amide and hydrogen by the combined catalytic action of the nickel of the boat and the solid sodium amide. To collect and measure this hydrogen the ammonia in the reaction tube was evaporated into a nitrometer containing dilute acid. The washings of the fusion, which contained metallic sodium, sodium amide and magnesium amide [the latter in the form of sodium ammono magnesiate, $Mg(NH_2)_2 \cdot 2NaNH_2$] were sealed off from the rest of the reaction tube and weighed, after drying in a vacuum.

When water was admitted to the specimen tube to hydrolyze its contents, considerable hydrogen pressure was developed. If this gas were allowed to escape into the atmosphere, some ammonia would be lost, and since the exact amount of this ammonia was necessary in the calculations to follow, the released hydrogen was bubbled through dilute acid. The hydrolysate was then sucked from the reaction tube through this same dilute acid[1] (See Fig. 2), which was analyzed for nitrogen and magnesium. The weight of the sodium extracted is equal to the weight of the washings (Wt. of tube + sample, dried in a vacuum, less weight of tube empty and evacuated.) less the magnesium amide (calculated from the magnesium analysis) and the sodium amide (calculated from the nitrogen in excess of that present as $Mg(NH_2)_2$). The total amount of sodium liberated by the magnesium is equal to the amount extracted plus that converted to sodium amide during the washing. (Item 15) The following table is a summary of three determinations.

TABLE I

	I	II	III
(1) Wt. Na converted to amide	excess	2.5882	2.2059
(2) Wt. Mg introduced	0.0700	0.0833	0.0979
(3) Equivalent weight Na	0.1324	0.1576	0.1852
(4) Wt. solids extracted	0.2431	0.1024	0.1774
(5) Volume hydrogen, 0°, 760mm., cc.	34.0	36.7	21.9
(6) Corresp. wt. Na	0.0697	0.0752	0.0450
(7) Nitrogen analysis (grams)	0.0800	0.0069	0.0152
(8) Mg Analysis ($Mg_2P_2O_7$)	0.1148	0.0050	0.0238
(9) Magnesium amide, wt.	0.0581	0.0025	0.0120
(10) Nitrogen in $Mg(NH_2)_2$	0.0289	0.0013	0.0060
(11) Nitrogen in $NaNH_2$ (7)−(10)	0.0511	0.0056	0.0092
(12) Sodium amide, wt.	0.1424	0.0156	0.0256
(13) Total amides, wt. (9)+(12)	0.2005	0.0181	0.0376
(14) Wt. Na extracted (4)−(13)	0.0426	0.0843	0.1398
(15) Wt. Na liberated (6)+(14)	0.1123	0.1505	0.1848
(3) Wt. Na equivalent to Mg	0.1324	0.1576	0.1852

Magnesium and Potassium Amide. Four preparations were made by fusing small amounts of clean magnesium ribbon (0.08 g. in Prep. I to 0.40 gram in Prep. II) with an excess of potassium amide for periods of time ranging from one hour, Prep. I, to six hours, Prep. II. The high magnesium and low nitrogen analyses of preparation II are perhaps to be accounted for by an incomplete reaction of the primarily produced magnesium amide with the potassium amide, since there still remained some precipitate in the boat at the end of the fusion period.

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[1] In Fig. 2 is pictured the apparatus customarily used for removal of solutions from an ammonia tube (Franklin: J. Phys. Chem., **15**, 516 (1911), with the exception that the tube *C* terminates underneath the dilute acid in the flask. In operation, suction is applied at *D*, and the solution in *A* is slowly drawn through the acid in *E*. *B*, *C* and *D* are then closed. *A* is removed and partly filled with water by opening stopcock B, with the end of the stopcock capillary under water. This solution is drawn through *E* in the same manner and the process repeated to ensure the complete removal of the specimen from *A*. The partial vacuum in *E* is released by slowly opening *C* and then *D* to the atmosphere.

Preparation 1. One half of 0.2660 gram gave 0.0442 g. nitrogen while the other half gave 0.0930 g. $Mg_2P_2O_7$. The preparation was dried in a vacuum at 20°.

Preparation 2. One fifth of 2.0944 g. gave 0.1364 g. nitrogen. A second fifth gave 0.3009 g. $Mg_2P_2O_7$ and a third fifth gave 0.7765 g. of a mixture of $MgSO_4$ and K_2SO_4. Dried in vacuo at 20°.

Preparation 3. The analytical data for this specimen has been lost. The analyses though are correctly reported.

Preparation 4. One quarter of 0.7162 g. (dried in a vacuum at 20°) gave 0.0560 g. nitrogen, while a second quarter gave 0.1347 g. $Mg_2P_2O_7$.

Calculated for $Mg(NHK)_2 \cdot 2NH_3$		Found I	II	III	IV
Mg	14.5	15.3	15.7	15.9	16.4
N	33.7	33.2	32.6	33.2	31.4
K	47.0		48.3 (indirect)		

Zinc and Potassium Amide. Preparation 1. Four tenths of a gram of fine zinc shot was added to fused potassium amide, but no immediate reaction occurred, other than a darkening of the color of the fusion. Some of the zinc was still unattacked after two hours. The washed specimen, insoluble in liquid ammonia, was light grey in color. The specimen, dried in a vacuum at 20°, weighed 0.0748 g. From this 0.0197 g. nitrogen was obtained.

Preparation 2. This was a duplicate of the preceding, except that the fusion was continued for four hours. The specimen, dried in a vacuum at 20°, weighed 0.6722 g. One quarter gave 0.0446 g. nitrogen and a second quarter gave 0.1247 g. $Zn_2P_2O_7$.

Calculated for $Zn(NHK)_2 \cdot 2NH_3$		Found I	II
N	27.0	26.3	26.6
Zn	31.4		31.8

Cadmium and Potassium Amide. Cadmium in the liquid form (temperature of fusion 400°!) is very slightly attacked by fused potassium amide in a period of two hours.

Aluminum and Potassium Amide. Preparation 1. Upon adding 0.29 g. of aluminum wire to molten potassium amide there was an immediate reaction with the production of a blue melt. After five hours of heating there still remained a good deal of the aluminum. In an ammonia tube the white insoluble matter was separated from the aluminum wire and the former prepared for analysis. Subs., dried in vacuo at 20°, 0.1954 g. Heated in vacuo at 130°, 0.1943 g. One half gave 0.0323 g. nitrogen and the other half gave 0.1060 g. Al_2O_3 and 0.0208 g. K_2SO_4.

Preparation 2. In this experiment—a duplicate of the preceding—small globules of potassium could be seen on top of the melt after addition of the aluminum. During the fusion a grey precipitate appeared in the melt and with time increased in amount. Time of fusion, five hours. The specimen, dried in a vacuum at 210°, weighed 0.2499 gram. One half gave 0.0400 g. nitrogen, while the other half gave 0.1334 g. Al_2O_3 and 0.0372 g. K_2SO_4.

Preparation 3. One half of 0.1056 g. (dried in a vacuum at 20°) gave 0.0164 g. nitrogen while the other half gave 0.0502 g. Al_2O_3 and 0.0261 g. K_2SO_4.

Calculated for	N	Al	K
AlN	34.2	65.9	0.0
$Al(NH_2)NHK$	37.1	23.9	34.6
Found			
I	33.0	57.5	9.6
II	32.0	56.6	13.4
III	31.0	50.4	22.2

Cerium and Potassium Amide. A half gram fragment of cerium dissolved in part in molten potassium amide (blue solution) and the liquid ammonia extraction gave a small amount of a grey precipitate, whose analysis did not correspond to a definite compound.

Thallium and Potassium Amide. Thallium, molten at the temperature of the fusion, 400°, was not attacked in four and one half hours.

Titanium, Zirconium, Thorium and Potassium Amide. Of these elements, the first two were not attacked at all in four hours. A short length of thorium rod (0.64 g) lost 20 mg. after five hours contact with fused potassium amide.

Germanium and Potassium Amide. Thirty and three tenths milligrams of germanium powder, prepared by reducing germanium oxide with hydrogen at 500°, was added to cold potassium amide and the mixture heated. Shortly afterward there was a vigorous evolution of gas which continued more slowly for one and one half hours and then ceased. The boat was examined at this time and found to contain a yellow solid with a clear supernatant liquid. The cooled melt was white and disintegrated readily in liquid ammonia to give a copious fine white precipitate. This was washed well with liquid ammonia but during the process it appeared to undergo a slight ammonolysis, as was inferred from the continued pale yellow or green color of the washings. (potassium amide in solution). Subs., dried in a vacuum at 20°, 0.5174 g. Heated in a vacuum at 110°, 0.5111 g. One quarter gave 0.0243 g. nitrogen. One half gave 0.1439 g. K_2SO_4. The germanium was separated by the method of Johnson and Dennis.[1] 190.2 cc of gases (standard conditions), collected during the fusion, consisted of hydrogen and nitrogen in the ratio of 13.69 to 1. Since the nitrogen was formed by the decomposition of ammonia in the presence of nickel and the fused amide, we must subtract the corresponding volume of hydrogen ($3 \text{x} \text{Vol. } N_2$) plus the volume of nitrogen from the collected gases (190.2 cc) in order to find the hydrogen actually formed in the reaction between germanium and potassium amide. (138.4 cc.)

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[1] Johnson and Dennis: J. Am. Chem. Soc., **47**, 790 (1925).

Preparation 2. This was a duplicate of the preceding experiment except that 0.332 g. germanium was used. The preparation, dried in a vacuum at 20°, weighed 0.3433 g. Heated in a vacuum at 210° it lost 0.0082 g. One fifth of the heated specimen gave 0.0107 g. nitrogen, a second fifth gave 0.0109 g. nitrogen, and two fifths gave 0.0851 g. K_2SO_4. The gases (348.3 cc.) collected during fusion consisted of hydrogen and nitrogen in the volume ratio of 6.918 to 1, that is, there was 172.3 cc. or 0.0155 g. hydrogen in excess of that arising from the decomposition of the amide.

	Ge	N	K	H:Ge[1]
Calc. for $Ge(NH)NK)$	51.6	19.9	27.8	4:1
" " $Ge(NK)\cdot NH_3$	50.8	19.6	27.4	2:1
Found I		19.8	25.0	2.96:1
" II		17.7	27.8	3.36:1

The analyses refer to the specimens dried in a vacuum at room temperatures.

Tantalum and Potassium Amide. Sheet tantalum was not attacked at all by fused potassium amide in six hours.

Chromium and Potassium Amide. In two experiments chromium in the form of small lumps was fused with potassium amide for three hours, but the solutions obtained by hydrolyzing the melt and then acidifying gave no tests for chromium.

Manganese and Potassium Amide. Fused potassium amide attacks manganese (prepared by the thermite process) rather superficially over a period of six hours. The melt is colored a light brown. A small amount of precipitate, sparingly soluble in liquid ammonia, blackened in contact with the air, a behavior characteristic of potassium ammono hypomanganite,[2] $Mn(NHK)_2\cdot 2NH_3$.

Manganese and Sodium Amide. Manganese is only slightly attacked by fused sodium amide, but the cooled melt imparts a yellow color to liquid ammonia indicating the formation of some sodium ammono hypomanganite.

Summary

(1) An apparatus and technique have been developed for studying the reactions of the fused alkali amides.

(2) In general, the reactions of the electropositive elements with the fused amides are similar to the same reactions in liquid ammonia at room temperatures. The strongly electropositive elements react initially with the fused amides to liberate free alkali metal.

(3) Magnesium, beryllium, zinc and calcium dissolve in the alkali amides to give the corresponding ammono metallate. (i.e. compounds analogous to

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[1] (Ratio of hydrogen evolved to the germanium reacting.)

[2] Bergstrom: J. Am. Chem. Soc., **46**, 1553 (1924). It is better to call this derivative of divalent manganese a hypomanganite, rather than a manganite as was done in the article referred to.

potassium zincate, $Zn(OK)_2$.) Germanium appears to be converted to a mixture of potassium ammono germanite and germanate by fused potassium amide. Cerium, thorium and manganese are slightly attacked by fused potassium amide, while copper, cadmium, mercury, thallium, titanium, zirconium, tantalum, chromium, nickel, platinum and iridium are not attacked after several hours fusion.

(4) Sodium dissolves in fused sodium hydroxide to give a blue colored melt.

(5) The course of the reaction of the strongly electropositive metals with the fused alkali hydroxides appears to be essentially the same as that with the fused alkali amides.

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A PHYSICOCHEMICAL STUDY OF THE CARBOHYDRATE OCCURRING IN THE ROOT OF ARCTIUM LAPPA

BY JOHN C. KRANTZ, JR. AND C. JELLEFF CARR

Introduction

Arctium Lappa (Burdock) is a coarse biennial weed which proliferates in Europe, Asia and North America.[1] The roots of this plant form a part of the vegetable portion of the Japanese dietary. The moist roots are sliced and cooked in fat.[3] The authors[4] have shown the carbohydrate to be absorbed and utilized by white rats as evidenced by increased glycogen storage in the liver. This fact was demonstrated also by showing that the root of Arctium Lappa exhibited a nitrogen-sparing action on dogs fed on a diet of protein. Its clinical value in the treatment of diabetes mellitus has been shown by one of us (J.K.) with Silver and Cohen.[5]

The authors have separated the polysaccharide (presumably) inulin from the root and have subjected it to a physicochemical study. The literature contains many references to the work on the inulin from dahlia and Jerusalem artichoke, but no reference was found to the properties of inulin from this source.

Tanret[6] investigated the physical and chemical properties of the inulin from Jerusalem artichoke and found the substance to consist of inulin, pseudo-inulin and inulenin. The value of the Jerusalem artichoke in the treatment of diabetes mellitus as evidenced by the classical experiments of Root and Baker[7] and also Carpenter and Root[8] stimulated a renewed interest in the properties of the carbohydrate from this root. Thus Irvine and Steele[9], Drew and Haworth[10] and also Haworth and Learner[11] have conducted recently extensive experiments on the structure of inulin from dahlia and the hydrolytic cleavage of this carbohydrate.

Furthermore, Jackson et al.[12] have studied the rate of hydrolysis of the artichoke inulin in their comprehensive investigations on the preparation of levulose.

A. Extraction of the Polysaccharide

The air-dried roots of the Arctium Lappa contain from 50 to 70 per cent of carbohydrate hydrolyzable into levulose. The dried root is reduced to about a No. 40 powder and extracted with ten volumes of boiling water. The aqueous extract is treated with a slight excess of solution of lead subacetate to precipitate the gums and resins. The filtrate is freed from lead salts by treatment with hydrogen sulphide. After filtration the solution is set aside at room temperature for several days until the separation of the carbohydrate is complete. The faintly yellow powder is separated by filtration and purified by dissolving in a small volume of hot water and precipitating with alcohol. By repeating this precipitation process three times, a completely white powder is obtained. The substance is washed with alcohol and dried to a constant weight in a vacuum desiccator at 38°C. This inulin containing from 0.15 to 0.2 per cent of ash was employed in these studies.

B. Optical Rotation

At 28° the specific rotation of the inulin from Lappa was $[\alpha]_D$ −34.7°. The rotation was observed in solution containing 8 gm. of the carbohydrate in 100 cc. in a 200 mm. tube.

Although inulin requires heat for solution in water, it is readily soluble in alkali hydroxide solutions. Under the same conditions a solution of the substance in normal sodium hydroxide solution showed a $[\alpha]_D$ of −34.7°.

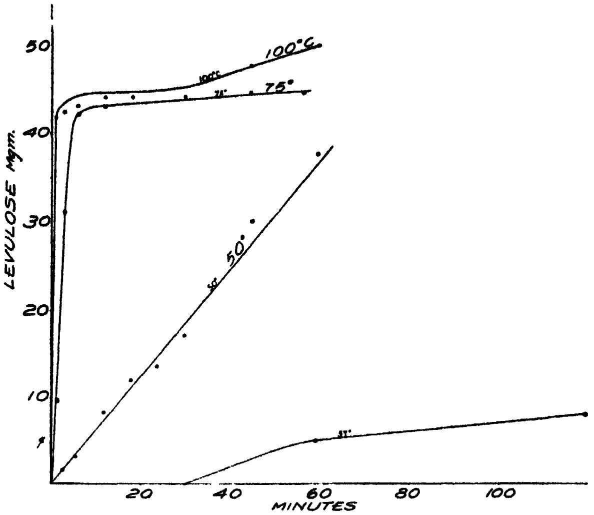
C. Hydrolysis—Influence of Temperature

The conditions under which the hydrolysis of inulin into levulose occurs is a matter of special importance in the utilization of this substance as a substitute carbohydrate in the treatment of diabetes. Okey[13] experimenting with the inulin from the Jerusalem artichoke, showed that this substance was partially hydrolyzed by the hydrochloric acid of the stomach and further this work demonstrated the presence of an inulase in the feces of normal patients fed a general diet.

TABLE I

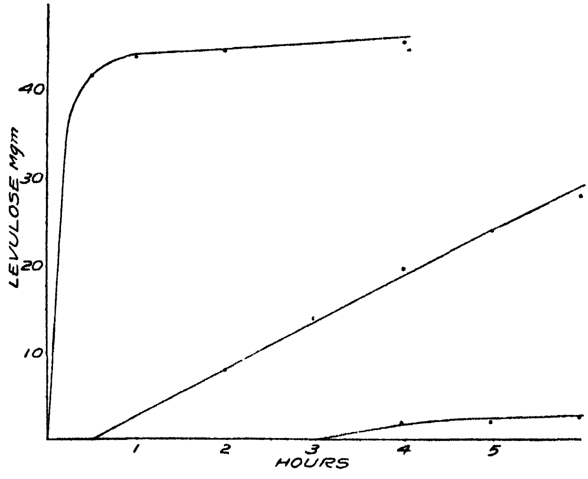
Hydrolysis of Inulin by Tenth-Normal Hydrochloric Acid at Various Temperatures

Temp.	Time min.	Levulose mgm.	Temp.	Time min.	Levulose mgm.
100°	1	41.9	75°	1	9.6
"	3	42.3	"	3	31.2
"	6	43.2	"	6	42.6
"	12	44.1	"	12	43.2
"	18	44.1	"	18	44.6
"	30	44.1	"	24	44.6
"	45	47.5	"	30	44.6
"	60	50.2	"	45	44.6
			"	60	44.2
50°	1	0.0	37°	30	0.0
"	3	1.5	"	60	5.1
"	6	3.0	"	120	8.2
"	12	8.2	"	180	14.1
"	18	11.8	"	240	19.9
"	24	13.1	"	300	24.0
"	30	17.2	"	360	28.6
"	45	30.8			
"	60	38.7			



Graph I

Influence of temperature upon the speed of hydrolysis of Inulin by 0.1N. HCl.



Graph II

Influence of concentration of HCl upon speed of hydrolysis of Inulin at 37°C.

The present authors studied the speed of hydrolysis of inulin from Burdock root as influenced by temperature and by concentration of acid.

Solutions of inulin in water (50 mgm. in 10 cc.) contained in tubes were placed in a constant temperature bath. Sufficient hydrochloric acid was added to make the total acid concentration tenth normal. After various time periods the hydrolysis was discontinued by the addition of sodium hydroxide solution. The reducing sugar formed was then determined by the Munson-Walker[14] method.

TABLE II

Influence of Concentration of HCl upon the Speed of Hydrolysis of Inulin at 37°C

Conc. HCl	Time min.	Levulose mgm.	Conc. HCl	Time min.	Levulose mgm.
1N.	30	41.8	0.1N.	30	0.0
1N.	60	44.1	0.1N.	60	5.1
1N.	120	44.7	0.1N.	120	8.2
1N.	240	45.6	0.1N.	240	19.9
0.01N.	180	0.0			
0.01N.	240	2.1			
0.01N.	300	2.1			
0.01N.	360	2.6			

Tables I and II show the results of these determinations which are also plotted in Graphs I and II.

The influence of various concentrations of hydrochloric acid upon the speed of hydrolysis is shown in Graph II.

D. Inversion Velocity Constant of Inulin from Burdock at 50°

Eight grams of inulin was dissolved in water and after adjusting the temperature to 50°, 10 cc. 1N. HCl was added and the solution was immediately made up to 100 cc. with water heated to 50°. Ten cc. portions of this solution were examined polariscopically at 30° after checking the hydrolysis by the neutralization of the acid.

The following general modification of the equation of a molecular reaction was employed:

$$K = 1/t \log_{10} \frac{R_0 - R_\infty}{R_t - R_\infty}$$

in which, R_0 is the reading before hydrolysis, R_∞ the reading after complete hydrolysis and R_t the reading at the time t. Table III shows the results of these determinations.

TABLE III

Inversion Velocity Constant

Time Min.	Rotation	Rt − R	$1/t \log_{10} \frac{R_0 - R_\infty}{R_t - R_\infty}$
0	−3.6	—	—
10	−4.4	3.5	8 94 × 10^{-3}
20	−5.0	2.9	8.56 × 10^{-3}
30	−5.6	2.3	9.06 × 10^{-3}
40	−6.1	1.8	9.45 × 10^{-3}
50	−6.4	1.5	9.16 × 10^{-3}
60	−7.9	1.2	9.24 × 10^{-3}
		Mean	9.07 × 10^{-3}

For a series of five determinations under the same conditions the velocity constant of Coleman and Bell's C.P. inulin obtained from dahlia was 9.3×10^{-3}.

These data indicate that the hydrolysis of the inulin from Burdock follows essentially the course of an unimolecular reaction. Jackson et al.[12] found this condition to hold for hydrolysis of the carbohydrate in the expressed juice of the Jerusalem artichoke tubers.

E. Cryoscopic Measurements

A sample of inulin was dissolved in water using as little heat as necessary to effect solution. The concentration was 5 gm. in 25 gm. of water. The depression of the freezing-point of water produced by the presence of inulin as determinated by the Beckmann cryoscopic apparatus is given in Table IV.

TABLE IV

Cryoscopic Measurements

No. 1	0.19°	No. 4	0.23°
2	0.24°	5	0.26°
3	0.26°		
		Mean	0.24°

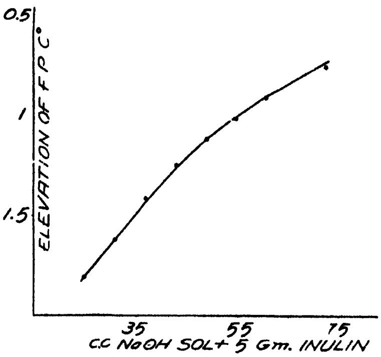
In the same concentration the mean depression of the solution of inulin from dahlia was determined to be 0.20°. Pringsheim and Fellner[15] determined the molecular weight of inulin from the dahlia tubers by direct measurement of the freezing point of its aqueous solution. They indicate that the molecule is composed of seven anhydrofructose units, which corresponds to a molecular weight of 1134. Drew and Haworth[10] by the boiling point method found the molecular weight of dahlia inulin to be 4000 in 4 minutes and to reduce regularly as the time increased being approximately 1200 in 17 minutes.

Using the well-known formula

$$M = \frac{C\ 100\ W}{\Delta w}$$

the present authors find the molecular weight of inulin from Burdock root to be 1550. Tanret[6] determined the molecular weight of inulin to be 4,827. We do not attach much significance to these data as actual molecular weights, yet it is of special interest to note that Tanret's molecular weight value for Inulenin from the Jerusalem artichoke is 1645 which agrees reasonably well with the value obtained with Burdock inulin.

Although it is generally supposed that levulose-free inluin will not reduce Fehling's Solution, in the experience of the authors it was quite impossible to obtain an inulin from Arctium Lappa which would not reduce the copper reagent after boiling for a short period (1.5 to 2 min.). Drew and Haworth[10] record the same experience and suggest that this reduction may be due to the presence of open-chain molecules initially present, augmented by hydrolysis. In the preparation of the solutions for cryoscopic measurements heat must be employed to effect solution and invariably these solutions reduced the boiling copper reagent indicating partial degradation. Thus it is doubtful whether the values obtained even approximate the actual molecular weight of this substance. It was observed, however, that when solutions of the inulin from dahlia were prepared much more heat was required to effect a clear solution (85° to 95°) than was necessary in the case of dissolving of the inulin from Burdock root (65° to 75°). It is not unlikely that this physical property indicates a difference in molecular complexity. As mentioned before, inulin dissolves in alkali solution (solution gives a definite Tyndall cone) in the cold, hence, it was thought interesting to determine the action of dissolved inulin upon the freezing point of sodium hydroxide solution. Five grams of inulin were dissolved in 25 cc. of 1N.NaOH solution and freezing points of the diluted solutions determined. These results are given in Table V.



Graph III

Effect of dissolved Inulin upon the freezing point of N.NaOH.

Table V

Effect of Dissolved Inulin from Burdock upon the Freezing Point of 1 N. NaOH

No.	Gm. Inulin	cc. NaOH sol.	diff.
1	5	25	+ 1.82°
2	5	31	+ 1.61°
3	5	37	+ 1.41°
4	5	43	+ 1.25°
5	5	49	+ 1.13°
6	5	55	+ 1.03°
7	5	61	+ 0.93°
8	5	73	+ 0.79°
9	5	125	+ 0.60°

These data are plotted in Graph III definitely indicating that the elevation of the freezing point of a sodium hydroxide solution is a function of the concentration of inulin dissolved therein.

In another series of cryoscopic measurements, the influence of varying concentrations of sodium hydroxide upon a constant concentration of inulin was determined. These data are given in Table VI.

TABLE VI

Effect of Changes in Concentration of NaOH upon the Freezing Point of Inulin Solutions

No.	Inulin Gm.	Solvent cc.	diff.
1	1	25 cc. 1 N.NaOH	+0.60°
2	1	25 cc. 0.1 N.NaOH	+0.11°
3	1	25 cc. 0.01 N.NaOH	0.00°
4	1	25 cc. 0.001 N.NaOH	−0.02°

These results seem to indicate that in sodium hydroxide solutions between 0.1 N. and 1 N. concentration that inulin from Burdock enters into compound formation thus reducing the number of particles in solution. In concentrations of 0.01 N. sodium hydroxide and below this there seems to be no evidence of compound formation as shown by the freezing point determinations.

Nef[16] in his comprehensive studies of the action of alkalies upon monosaccharides postulates that these substances may react with oxygen to form acids. This investigator claimed that a solution of glucose in sodium hydroxide yields an equilibrium mixture of at least 93 different compounds. In view of the results obtained by the freezing point determinations of alkali solutions of the inulin from Burdock, it is not unlikely that the high hydroxyl-ion concentration causes a partial degradation of the inulin molecule into alkali consuming substances.

F. The Buffer Capacity of the Inulin from Burdock

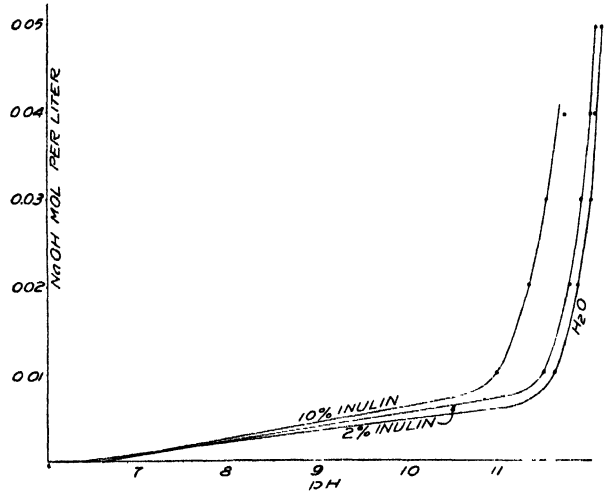
From the foregoing results of the cryoscopic measurements and in view of the work of Michaelis and Rona[17] who thru the determination of the dissociation constants of sugars, considered them as weak acids, the authors were prompted to determine the buffer capacity of this carbohydrate against alkalies. The method employed was devised by Van Slyke[18] and employed by one of the authors to measure the buffer capacity of acacia, tragacanth[19] and the extractive of digitalis leaves.[20] The pH values were measured electrometrically using a Wilson[21] electrode.

Graph IV shows the results of this experiment.

The solutions of the polysaccharide showed little capacity to change the hydroxyl-ion concentration of the alkaline solutions. With 10 per cent inulin solution pH 6.60 the addition of 0.01 mole of sodium hydroxide per liter changed the hydrogen-ion concentration to pH 11.06—in water pH 6.40 the same amount of alkali changed the pH to 11.55. For the 10 per cent inulin solution

$$\frac{\Delta B}{\Delta pH} = \frac{0.01}{4.46} = 0.002$$

As the curve between pH 6.60 and 11.06 is a straight line the "Van Slyke B" which is the differential ratio dB/dpH will have the same value.



GRAPH IV
Buffer capacity of Inulin from Burdock

Summary

Certain physicochemical characteristics of the carbohydrate from Arctium Lappa have been determined. The substance has the essential characteristics of an anhydrofructose molecule.

Bibliography

[1] D. M. R. Culbreth: "Manual of Materia Medica and Pharmacology," 615.

[2] Digest of Japanese Investigations on the Nutrition of Man—Kintaro Oshima: U. S. Dept. Agric. Bull., No. 159, 40 (1905).

[3] Inazo Nitobe: Am. J. Pharm., **72**, 416 (1897).

[4] J. C. Krantz, Jr. and C. J. Carr: in press.

[5] A. Silver, B. Cohen, and J. C. Krantz, Jr.: in press.

[6] C. Tanret: J. Pharm. Chim., **27**, 449 (1893); Compt. rend., **116**, 1143 (1893).

[7] Root and Baker: Arch. Int. Med., **36**, 126 (1925).

[8] Carpenter and Root: Arch. Int. Med., **42**, 64 (1928).

[9] J. C. Irvine and E. S. Steele: J. Chem. Soc., **117**, 1474 (1920).

[10] H. K. Drew and W. N. Haworth: J. Chem. Soc., **1928**, 2690.

[11] W. N. Haworth and A. Learner: J. Chem. Soc., **1928**, 2690.

[12]. R. F. Jackson, C. G. Silsbee, and M. J. Proffitt: Scientific Papers Bureau of Standards, U. S., No. 519, 587 (1926).

[13] Ruth Okey: J. Biol. Chem., **39**, 149 (1919).

[14] Munson and Walker: J. Am. Chem. Soc., **28**, 163 (1906).

[15] Pringsheim and Fellner: Ann., **462**, 231 (1928) through Drew and Haworth.

[16] J. U. Nef: Ann., **357**, 214 (1907); **403**, 204 (1914) through Gortner: "Outlines of Biochemistry," 519.

[17] L. Michaelis and P. Rona: Biochem. Z., **49**, 232 (1913).

[18] D. D. Van Slyke: J. Biol. Chem., **53**, 528 (1922).

[19] J. C. Krantz, Jr.: J. Am. Pharm. Ass'n., **18**, 469 (1929).

[20] J. C. Krantz, Jr.: J. Am. Pharm. Ass'n., **19**, 366 (1920).

[21] Wilson: Ind. Eng. Chem., **17**, 74 (1925).

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THE HYPOTHETICAL POTASSIUM POLYIODIDES*

BY WILDER D. BANCROFT, G. A. SCHERER AND L. P. GOULD

Professor Grinnell Jones[1] believes in the existence of potassium tri-iodide as a stable solid phase at 25°, and gives definite reasons for his belief. "Johnson[2] evaporated solutions of iodine and potassium iodide over sulfuric acid and obtained lustrous, dark prismatic crystals, some of which were over two inches long, which were proved by analyses to have the composition represented by KI_3. He also determined the density of these crystals to be 3.498, which corresponded to a molecular volume of 120.1 cc., whereas the molecular volume of KI is 54.3 cc. and of I_2 is 51.34 cc., making a total of 105.64 cc. Therefore, unless Johnson made an error of nearly 15% in the determination of the density of his crystals, they could not have been a mixture of potassium iodide and iodine. He found the melting point to be 45°C. Wells, Wheeler and Penfield[3] also prepared solid KI_3 and determined the crystal angles and showed that it is monoclinic and determined the melting-point to 38°C. Foote and Chalker[4] obtain evidence of the formation of solid KI_3 from Phase Rule studies of the system $KI\text{-}I_2\text{-}H_2O$. Clark and Duane[5] have prepared solid crystals of KI_3 and confirm the observation of Wells and Penfield that it belongs to the monoclinic system and have studied the structure of the crystal by means of X-ray analysis with results proving that their crystals were not merely a mixture of KI and I_2. It should be noted, however, that Johnson is the only one of these investigators who reports analyses of the pure crystals.

"But in spite of this definite and circumstantial evidence of the existence of solid KI_3, Abegg and Hamburger,[6] Parsons and Corliss,[7] Parsons and Whittemore,[8] and Bancroft[9] deny the existence of solid KI_3 at 25°C. on the basis of Phase Rule studies of the system $KI\text{-}I_2\text{-}H_2O$. Abegg and Hamburger and Foote and Chalker state that a higher complex having the formula KI_7 exists in the solid state at 25°C., whereas Parsons and his collaborators deny the existence of any solid polyiodides of potassium at 25°C.

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* The experimental work was done in 1927-1929 and part of it was reported on at the Swampscott meeting of the American Chemical Society in 1928. The present article was written in September 1930, after having read the manuscript by Briggs and Geigle: J. Phys. Chem., 34, 2250 (1930).

[1] J. Phys. Chem., 34, 684 (1930).

[2] J. Chem. Soc., 31, 249 (1877).

[3] Z. anorg. Chem., 1, 442 (1892).

[4] Am Chem. J., 39, 561 (1908).

[5] J. Opt. Soc. America, 7, 472 (1923).

[6] Z. anorg. Chem., 50, 427 (1906).

[7] J. Am. Chem. Soc., 32, 1367 (1910).

[8] J. Am. Chem. Soc., 33, 1933 (1911).

[9] W. D. Bancroft: oral statement before the Division of Physical Chemistry at the Swampscott meeting of the American Chemical Society, September 1928.

"Berthelot[1] obtained crystals which he believed to be KI_3 but he found the heat of solution of these crystals to be the same as the heat of solution of equivalent quantities of KI and I_2 in the same amount of water, which indicates but does not necessarily prove that his crystals were a mixture rather than a compound.

"There are numerous references in the literature describing complex solid polyiodides[2] of rubidium, cesium, ammonium, and organic bases.

"There is thus an irreconcilable conflict of evidence in the literature as to the existence of solid KI_3. There are reports of four independent investigations in which it is claimed that solid KI_3 was obtained and in one or more of these researches the chemical analysis, density, melting point, crystal system and crystal angles, and internal structure as deduced from X-ray analyses were determined. On the other hand there are four separate investigations based on Phase Rule studies of the system $KI\text{-}I_2\text{-}H_2O$ in which no evidence of the occurrence of KI_3 was found. The reviewer [Grinnell Jones] gives greater weight to the definite, circumstantial, positive evidence of the existence of solid KI_3 than to the negative evidence of those investigators who failed to find it. But even if it should eventually be definitely determined that KI_3 is unstable at 25°C., this fact—if it be a fact—would merely indicate that the vapor pressure of iodine from solid KI_3 exceeds that of pure iodine at 25°C; but would not disprove the existence of tri-iodide ions in solution. Evidence as to the existence of solid tri-iodides of cesium, rubidium and ammonium seems to be undenied. On the other hand, so far as the reviewer is aware, no one claims to have produced solid LiI_3 or NaI_3."

This is the strongest possible case that can be made out for the existence of potassium tri-iodide as a stable solid phase at 25°. The point at issue is whether phase rule methods are more or less reliable than other methods in this particular case. Before taking up that point, it will be well to eliminate the two sets of phase rule investigations which purport to show some such compound as KI_7. Professor Jones gives equal weight to Abegg and Hamburger, to Foote and Chalker, and to Parsons and his collaborators, which indicates an uncritical attitude.

Abegg and Hamburger studied the freezing-point curves for potassium iodide and iodine, and also determined the 25° isotherm for the ternary system $KI\text{-}I_2\text{-}H_2O$. Their data for the freezing-point curves are shown in Fig. 1, reproduced from the article by Briggs and Geigle.[3] Abegg and Hamburger found a eutectic at 80.5° and then a nearly horizontal branch, along which they assumed arbitrarily that KI_7 crystallized, because of what they assumed to be a maximum in the curve at or near the composition corresponding to KI_7. Since then, the true phase diagram has been determined by Briggs and Geigle and is shown in Fig. 2.

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[1] Compt. rend., 90, 841 (1880).

[2] J. W. Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 2, 609 ff. (1922).

[3] J. Phys. Chem., 34, 2250 (1930).

"AB and BF are the liquidus (or solubility) curves for iodine and potassium iodide, respectively. EF is the boiling point curve for unsaturated solutions of potassium iodide in liquid iodine at approximately one atmosphere (740 mm). CBD is the eutectic boundary line and GFH is a similar line for systems consisting of salt, solution and vapor—which must in this case be practically pure iodine since the vapor pressure of potassium iodide is virtually zero at this temperature. Above the latter line, all mixtures of the two components exist in the form of salt and vapor as coexisting phases, while in the triangular area EFG the coexisting phases are solution and vapor. The area AEFB, limited by the boundary lines AE, EF, FB, and AB, shows the conditions under which the two components exist as a single liquid phase—viz. as unsaturated solution. The remaining areas have their usual significance.

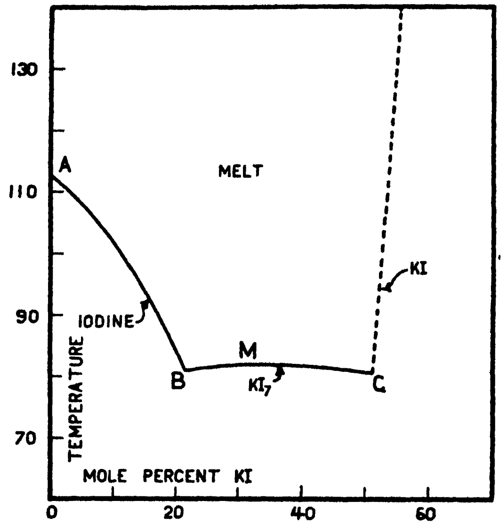

Fig 1

The System KI-I_2 according to Abegg and Hamburger

"The diagram as drawn applies, of course, to the system under a pressure of approximately one atmosphere. The lines AB and BF would be essentially the same for the system kept under the (variable) pressure of its own vapor, in which case the line BF could be followed upward either to the melting point of potassium iodide (680°) or to a critical point, the steepness of this line giving one reason to expect the latter. It is unlikely, however, that anything of importance would be learned by completing the diagram at high pressures and it would be in addition a difficult experimental problem.

"It is interesting to compare the present diagram—excluding the upper lines for systems in equilibrium with vapor—with the diagram as given by Abegg and Hamburger and by Kremann and Schoulz (Fig. 1). These investigators, for the reasons already given, missed entirely the real solubility curve for potassium iodide, and as the result took part of the eutectic line (BMC in Fig. 1) to be the solubility curve of a compound (KI_7 or KI_4). They also placed the solubility curve for potassium iodide (the broken line in Fig. 1) in a quite erroneous position, though this was admittedly a pure guess on their part. The work of these investigators is a striking example of the danger of relying entirely upon temperature arrests, uncorroborated by other tests, in determining a phase diagram.

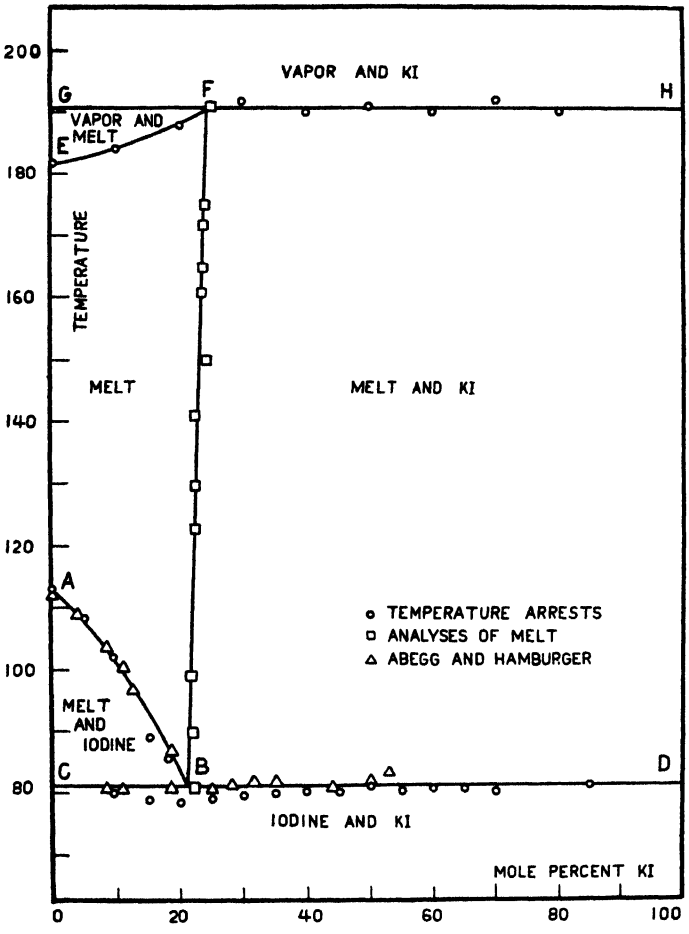

FIG. 2

Temperature-Composition Diagram for the System $KI-I_2$ at approximately 1 atm.

"The present work is of importance because of its bearing on the extremely controversial subject of the polyiodides of potassium. It proves definitely that there are no such polyiodides as stable phases in equilibrium with melt. Indeed, it may be stated that up to the present no one has presented strictly trustworthy evidence that a polyiodide of potassium exists as a solid.[1] In the case of cesium, however, the evidence for the existence of polyiodides[2] is definite."

The three sets of observers, Abegg and Hamburger, Kremann and Schoulz, and Briggs agree that the eutectic temperature for potassium iodide and iodine lies between 80° and 81°. This bars out the observation by Johnson that potassium tri-iodide melts at 45°, and the corresponding observation by Wells, Wheeler and Penfield that it melts at 38°. This had already been mentioned by Abegg and Hamburger.[3] "It is clear from the curves that no mixtures of iodine and potassium iodide melt below 80°. We must, therefore, recognize as false the melting-point determinations of Johnson[4] and of Wells and Wheeler[5] for KI_3, which gave melting-points of 45° and 38° respectively. Their preparations undoubtedly contained water. In fact we have observed a melting at 30° in the capillary for a pure sample crystallized from water, and one can force the melting-point of a potassium iodide-iodine mixture from 80° down to 40° merely by breathing on it." This was probably overlooked by Grinnell Jones.

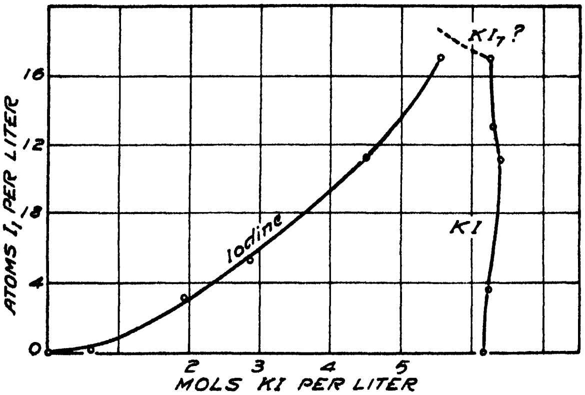

FIG. 3

Isotherm at 25° according to Abegg and Hamburger.

The data of Abegg and Hamburger for the 25° isotherm of potassium iodide and iodine in water are given in Fig. 3. Abegg and Hamburger make the two arbitrary assumptions that a new phase occurs along the dotted line and that its composition is KI_7. There is not a scrap of evidence for either assumption; but people have believed it because Abegg and Hamburger said it loud and clear.

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[1] Cf. particularly Parsons and Corliss: J. Am. Chem. Soc., **32**, 1367 (1910); Parsons and Whittemore: **33**, 1933 (1911).

[2] Cf. Briggs, Greenawald and Leonard: J. Phys. Chem., **34**, 1951; Briggs: 2260 (1930).

[3] Z. anorg. Chem., **50**, 435 (1906).

[4] J. Chem. Soc., **31**, 249 (1877).

[5] Am. J. Sci., (3) **43**, 475 (1892).

Abegg and Hamburger[1] have some experiments with potassium iodide, iodine and benzene which really look as though they had KI_7 as solid phase. They started with a concentrated solution of iodine in benzene, and added varying amounts of potassium iodide until the concentration of iodine had fallen to a constant value. Knowing the amount of potassium iodide added and the amount of iodine that had been taken out of the solution, they could of course calculate the composition of the solid phase, which was apparently KI_7. They recognized the danger of moisture as introducing a second liquid phase and worked in sealed vessels. Since Dawson[2] had shown that iodine does not make potassium iodide soluble in benzene, there is no error on that score. On the other hand it is known that iodine forms a solid solution with benzene. If iodine forms a solid solution with benzene as it may, it is impossible to reason from the behavior in benzene to the behavior in water, because the solid phases would not be the same in the two cases. Since the results of Abegg and Hamburger with benzene do not check those of Parsons and Whittemore and of Scherer with water, and since their results have not yet been checked by anybody, it is safer not to lay too much stress on them for the present. It is very unfortunate under the circumstances that Abegg and Hamburger should have deduced the equilibrium of KI_7 with aqueous solutions from their benzene experiments instead of from the experiments with water. This is the more unfortunate because they were entirely wrong in their melting-point determinations.

Foote and Chalker appear to have found KI_3 and KI_7 as solid phases in aqueous solutions and Grinnell Jones says that positive results should be given preference over negative results. That is true in some cases; but there is no evidence of any precautions having been taken by Foote and Chalker. If KI_3 and KI_7 crystallized from their solutions, nobody should have any difficulty in getting these compounds. Apparently they also took no especial precautions to reach equilibrium, whereas Parsons and Whittemore did. Our experiments confirm those of Parsons and Whittemore and consequently we are forced to believe that the data of Foote and Chalker are inaccurate.

We can now consider the data obtained by Parsons and Whittemore.[3] They prepared solutions saturated with either iodine or potassium iodide in the presence of varying amounts of the other. In order to determine the solubility curves and corresponding solid phases for the system potassium iodide, iodine and water, various mixtures were prepared and placed in 100 cc bottles which were rotated in a thermostat at 25°. From time to time the bottles were removed for analysis and for the addition of more potassium iodide or iodine as the case might require, should examination show that the solid phase had all disappeared. This was continued until equilibrium was reached, some of the bottles being shaken for several months when necessary.

When equilibrium was reached, as shown by duplicate analyses made many days apart, a portion of the solid phase with adhering mother liquor was removed and analyzed. The results were plotted as a solubility curve and the prolongation of the lines drawn through points representing the compositions of a solution and the corresponding points representing the compositions of the solid phases with adhering mother liquor meet in a point representing the composition of the solid phase, so long as there is present one solid phase of constant composition. At the quadruple point with two solid phases, solution phase, and vapor phase, the solution can be shown to be in equilibrium with either pure component or with any mixture of them. This work showed that the mutual solubility of potassium iodide and iodine, referred to a constant amount of water, increases with increasing amounts of each, though the percentage composition of potassium iodide in the ternary mixture decreases. At the quadruple point the solution phase contains about two and one-half mols of iodine per mol of potassium iodide.

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[1] Z. anorg. Chem., 50, 409 (1906).

[2] J. Chem. Soc., 85, 467 (1904).

[3] J. Am. Chem. Soc., 33, 1933 (1911).

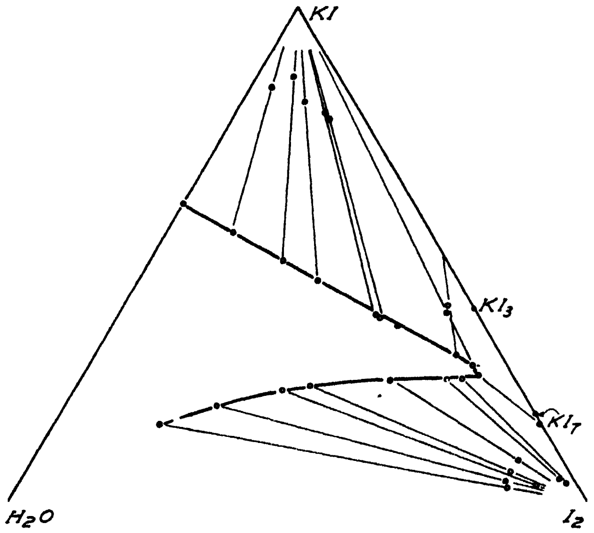

FIG. 4
The Mutual Solubility of I_2 and KI in H_2O.

Parsons and Whittemore assume that water does not enter into the composition of the solid phase and they plot their results on ordinary rectangular co-ordinates. There is no need of doing this and we have therefore plotted their data on a triangular diagram, Fig. 4, the numerical data being given in Table I.

There is evidently some mistake about the eighth analysis; but all the other data, including the ninth, show that potassium iodide and iodine are the only two solid phases. There is nothing that suggests KI_3, even remotely, not even the faulty No. 8. The eighteenth gives a solid phase corresponding pretty closely to KI_7—about 16 percent KI instead of about 18 percent; but this happens to be the quadruple point where the apparent composition of the solid phase can be varied at will from 100 percent iodine to 100 percent iodide. It was purely a coincidence that this particular experiment

TABLE I

Solubility of Iodine and Potassium Iodide in Water at 25°

Analysis of liquid phase			Analysis of solid phase with adhering mother liquor		
% KI	% I_2	% H_2O	% KI	% I	% H_2O
(a) In equilibrium with KI					
60.39	0.0	39.61	100.00	0.0	0.0
54.49	11.60	33.91	84.92	4.05	10.03
49.05	23.11	27.84	85.94	6.32	7.74
44.90	31.01	24.09	80.46	10.84	8.70
38.09	44.58	17.33	78.56	15.23	6.21
37.60	45.56	16.84	77.32	16.73	5.95
35.84	49.57	14.59	—	—	—
29.77*	62.81	7.42	39.99	56.10	3.91
27.86	66.48	5.66	38.78	56.27	3.95
(b) In equilibrium with iodine					
16.06	18.47	65.47	3.04	85.43	11.53
19.64	26.21	54.15	4.48	83.87	11.65
22.92	36.08	41.00	3.70	89.33	6.97
23.46	40.51	36.03	6.49	83.62	9.89
24.83	53.59	21.58	8.62	83.81	7.57
25.09	63.14	11.77	4.82	92.41	2.77
25.08	65.98	8.94	4.00	94.39	1.61

* [This one must be wrong so far as the solid phase is concerned.]

happened to come out with a composition approximately KI_7. Working as people often do, this solution could have been said to be in equilibrium with KI_7.

While these experiments would seem to be absolutely conclusive, there is one possible source of error. Let us assume, for the purposes of discussion, that potassium tri-iodide, though a stable phase, does not form readily and did not form in the experiments of Parsons and Whittemore. In that case a portion of their curve near the tip represents a metastable equilibrium. In that case the true isotherm consists of three branches as postulated by Abegg and Hamburger. This is not probable, because Johnson, Wells and Wheeler, and Foote and Chalker apparently took no particular pains and yet obtained what they called potassium tri-iodide. It is possible, however, and consequently an experiment was made to settle this question.

A solution corresponding approximately to the quadruple point on the curve of Parsons and Whittemore was made up synthetically. To this was added more potassium iodide and iodine so as to be certain of having an excess of both substances. The mixture was placed in a thermostat at 25° ± 0.1° and left there until the solution was in equilibrium both with the solid potassium iodide and the solid iodine. A titration of the saturated solution by means of a standard sodium thiosulphate solution showed that the composition of the solution was practically identical with that given by Parsons and Whittemore. That confirmed their result. We then added crystals of Johnson's so-called tri-iodide prepared as he had prepared them. If the solution in the thermostat was in metastable equilibrium, the concentration must change on being seeded with what purported to be crystals of the stable phases. If the solution in the thermostat was in stable equilibrium, addition of Johnson's crystals would cause no change regardless of what they were.

After waiting several days the seeded solution was analyzed and was found not to have changed in composition. The solution was analyzed by diluting a weighed portion of the solution to 100 cc with 95% alcohol and titrating an aliquot portion of this alcohol solution with a standard solution of sodium thiosulphate, using starch as an indicator. The results are given in Table II along with some of the data of Parsons and Whittemore for comparison.

TABLE II

Analysis of Saturated Solution of KI and I_2

	G. sol. taken	Aliquot part	cc $Na_2S_2O_3$	% I_2	Mean
	Solution before adding crystals:				
Dec. 14	2.4986	1/10	40.57	62.75	
Jan. 17	3.1762	1/10	53.29	64.87	
Feb. 15	6.2972	1/10	106.18	65.19	65.19
Mar. 2	3.6352	1/10	61.29	65.19	
Parsons and Whittemore				68.13	
	Solution after adding crystals:				
Mar. 8	2.3779	1/10	40.09	65.18	65.19
Mar. 13	1.8783	1/10	31.67	65.19	

$Na_2S_2O_3$ = 0.30461 N

There is therefore no potassium tri-iodide as stable solid phase at 25° any more than there is in equilibrium with the melt. This being so, Johnson, Wells and Wheeler, and Clark either did not have potassium tri-iodide at all or had a metastable phase. This last does not seem probable.

Johnson states that he succeeded in obtaining lustrous, dark blue, prismatic crystals by evaporating slowly over sulphuric acid concentrated solutions of iodine in aqueous potassium iodide, which analysis showed to be the tri-iodide. He determined the KI by gentle heating of the crystals (dried over sulphuric acid) until potassium iodide alone remained. Then "in order to effect a more direct determination of the iodine, the crystals were dissolved in a little water (containing some potassium iodide to prevent precipitation of iodine) and the amount of the latter in excess of that required for the iodide was determined by a standard solution of sodium hyposulphite, starch being used as indicator." The specific gravity of these crystals was found to be 3.498. The same compound has been obtained by Wells and Wheeler[1] and its crystallography determined.

Johnson describes KI_3 as "long prisms which are almost black, and exhibit a lustre resembling that of iodine; it is extremely deliquescent, and can be preserved only in an atmosphere dried by sulphuric acid; when it is exposed to ordinary air, a film of moisture is immediately deposited, the gradually increasing thickness of which causes a rapid succession of colors resembling those formed in the tempering of steel. After a short time it becomes a brown liquid. If crystals are exposed to light for even a few minutes, and then again allowed to dry over sulphuric acid, a film of potassium iodide, due to the efflorescence of iodine, forms on their surface, destroying their metallic lustre and after two or three repetitions of such treatment, even producing a whitish crust of that salt, which, however, exerts a protective influence upon the tri-iodide beneath."

Crystals the same as those described by Johnson and by Wells and Wheeler have been prepared according to the methods outlined by these authors. Solutions made by dissolving iodine and potassium iodide in the proportion of 60.4 iodine to 39.6 potassium iodide in as little water as possible were evaporated slowly over sulphuric acid at a low temperature. Due to the extremely deliquescent character of the crystals, it is impossible to transfer them from the desiccator to the balance without an increase in weight due to the absorption of moisture. There may also be water or mother liquor contained in minute cavities in the crystals. These crystals were dried from the mother liquor with filter paper, weighed quickly, and analyzed. The weighed crystals were dissolved in dilute aqueous potassium iodide and the free iodine determined by a standard solution of sodium thiosulphate, using starch as an indicator. Another weighed portion of the crystals was heated gently until potassium iodide alone remained and this white residue was then weighed. The analyses showed the crystals to have approximately the composition of KI_3, which is in agreement with the analyses of Johnson. The data are given in Table III along with some of the analyses of Johnson for comparison. The crystals used for the three samples are from three different crystallizations. The fact that the iodine and potassium iodide percentages do not add up to a hundred shows that the crystals were not perfectly dry. This was recognized by Johnson.

Our results agree with Johnson's theory even better than his own do and much better than they should considering the peculiar properties of the crystals. There was no conceivable reason why Johnson or those who followed him should have questioned the existence of a solid potassium tri-iodide.

On the other hand Parsons and Whittemore found that no potassium tri-iodide crystallized along the whole isotherm and our experiments, already cited, showed that there is no stable tri-iodide. Consequently, Johnson's crystals either represented a metastable phase or there is something wrong

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[1] Am. J. Sci., (3) **43**, 475 (1892).

TABLE III

Analyses of Crystals (KI_3)

	grams sample	% KI	grams sample	% I_2	Ratio KI/I_2
Sample 1	0.0393	37.15	0.0695	57.49	
Sample 2	0.1654	37.19	0.0599	57.91	
Sample 3	0.0618	36.89	0.0968	57.70	
Mean		37.08		57.70	1.002
Johnson 1	0.789	37.90	0.66	58.94	
Johnson 2	0.717	36.96	0.762	58.67	
Mean		37.43		58.80	0.973

in the analyses. It does not seem probable that Johnson's crystals were metastable, because he says that "the crystals first deposited were dark-coloured cubes, which proved to be potassium iodide, coloured by a little free iodine; but after some days, lustrous dark-blue prismatic crystals, sometimes two inches long, were deposited, which had the composition required by the formula KI_3." One would hardly expect a metastable form to come out in presence of potassium iodide crystals.

As these crystals came out of solution in long needles in much the same way that potassium iodide crystallizes out of a supersaturated solution of potassium iodide under special conditions, this seemed to tie in with the results of Parsons and Whittemore. If the crystals are really potassium iodide colored with iodine, the question comes up why the crystals should analyze as KI_3 if they are essentially potassium iodide. The mother liquor is richer in iodine relatively to potassium iodide, which would bring the iodine content too high. The more serious difficulty is that drying between filter paper removes relatively more potassium iodide than iodine. If this is the case, an analysis of wet crystals should show less iodine than an analysis of dried crystals. The data illustrating this are given in Table IV.

TABLE IV

Analysis of Wet Crystals

% KI	% I_2	Ratio KI/I_2	
35.2	44.1	1.92 wet	1.00 dry
31.0	45.2	2.22 wet	
From Table III			1.00 dry

We have here the extraordinary phenomenon that the wet crystals contain less iodine than the dried crystals, even though the mother liquor contains much more iodine relatively than the crystals. It is of course an unfortunate coincidence that the analysis of the dried crystals should have come out so close to KI_3. The odds are almost anything one pleases against this happening; but it did. The discovery of this remarkable and entirely unexpected error means that the only analyses of the solid phases which have any value show the solid phases to be potassium iodide and iodine.

If there is no solid potassium tri-iodide, there must be something wrong with the experiments by Wells, Wheeler and Penfield.[1] They accepted Johnson's analysis and their melting-point of 38° was seven degrees below that which Johnson found and at least 42° below what seems to be the lowest possible melting point for the system. These are natural errors; but it does not seem possible that they could have slipped up on their crystallographic data, and yet they apparently did. It is also possible that people have overestimated in the general discussion the magnitude of the difference between a cubic and a monoclinic crystal. If the potassium iodide from the iodine solution contains a little iodine in solid solution, as it may well do, that might be enough to change one of the axes slightly. It should be kept in mind that all that Wheeler and Wells have done was to show that the crystals that they examined differed slightly from potassium iodide. They accepted Johnson's inaccurate analysis without question and without proof. There is really nothing in their work to show that they were studying potassium tri-iodide and we know that they were not. The crystals come out either as columns, which may be cubes in a row, or as needles. Qualitatively similar types of crystals can be obtained from potassium iodide solutions containing no iodine under suitable conditions and the only possible conclusion is that the crystals are potassium iodide colored by iodine and that Wells, Wheeler and Penfield were misled by the assumed analogy with cesium iodide.

As a matter of fact, Briggs[2] has shown that Wells[3] and his co-workers slipped somewhat in their work on cesium iodide and iodine. "Wells and Penfield stated that cesium tri-iodide melts at 210° and 'whitens' through loss of iodine at 330° when heated in an open tube. It is apparent from the diagram [Fig. 4] that they were right enough about the 'melting' point, although the melting of course was not complete. The 'whitening' temperature, however, was placed too high, since the iodine may be boiled out completely at about 303°.

"Wells and Wheeler, in describing the higher polyiodide which they took to be CsI_5, stated that it melted at 73°; but they also remarked—and this puzzled them greatly—that mixtures of iodine and cesium iodide between CsI_4 and CsI_9 likewise melted at 73°. It is apparent from the diagram that the temperature referred to as a melting point by Wells and Wheeler is actually the eutectic temperature for iodine and polyiodide as solid phases. Accordingly, their mixtures of the two components could not have melted completely in general as they thought—that is to say, these investigators made the same mistake that Abegg and Hamburger and Kremann and Schoulz made at a later date in the case of iodine and potassium iodide. They mistook the eutectic for a melting point.

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[1] Am. J. Sci., (3) **43**, 475 (1892).

[2] J. Phys. Chem., **34**, 2260 (1930).

[3] Wells and Penfield: Am. J. Sci., (3) **43**, 17 (1892); Wells and Wheeler: **44**, 43 (1892).

"We can go still farther, in addition, and say with confidence that, since Wells and Wheeler gave 73° as the melting point of the higher polyiodide, they could not have prepared it pure. They really had a mixture of the higher polyiodide and iodine, and for this reason the analyses which they made in an attempt to establish the formula of the polyiodide are worthless. They do give the clue to the correct formula, however; but it lies hidden in the statement that mixtures on the iodine side of CsI_3 melt always at 73°. This is precisely what the present investigation has shown to be the upper limit for the first eutectic and is additional evidence to prove that the higher polyiodide is unquestionably CsI_4. It is most interesting to find this bit of evidence tucked away in the original paper of Wells and Wheeler."

We have still to consider the X-ray determinations by Clark and Duane.[1] "With the new method of crystal structure analysis established in its fundamental features by the study of KI, its extension to the more complex structures of secondary valence compounds followed. It seemed logical to select potassium tri-iodide, not only because of its close relationship as a polyiodide to KI, but also because of its great chemical interest and importance in such matters as iodometric analysis, etc.

"Splendid crystals of convenient size and thickness for transmission experiments separated after very slow spontaneous evaporation *in vacuo* from a strong aqueous solution containing theoretical quantities[2] of KI and iodine. Without a very careful control of the evaporation, a mud of indefinite composition[3] precipitated. Since the vapor pressure of iodine from the compound reaches 760 mm in an enclosed space at 146°C, it became necessary during the analysis to protect the crystal against rapid loss of iodine by enclosing it in a very thin glass bulb mounted on the crystal table.

"The analysis proceeded in exactly the same way as outlined for KI. In the determination of the angles between planes, peak reflections occurred at angles of almost 90° and 45° from the peak for the 100 reflections. The angular reading for the 100 peak was 45°48′, and for the 100 peak 0°30′. This slight departure of about 18′ from perfect cubic symmetry verifies the discovery by Wells and Penfield in goniometric measurements that one of the axes is slightly inclined to the plane containing the other two at right angles. The experiments indicate, therefore, a cube slightly distorted into a monoclinic prism. The critical voltage for the 100 peak produced by transmission through the crystal approximated 11,300 volts at an angle, θ, of 6°45′, corresponding to the wave-length 1.09Å. Substituting this value in the equation $\lambda = 2\ d \sin \theta$, gives $d_{100} = 4.68 \times 10^{-8}$ cm. The number of molecules per unit, calculated from $m = \rho d^3/Ww$, where ρ, the density, is 3.398, W, the molecular weight is 419.86 and w, the weight of the hydrogen atom, is 1.663×10^{-24}, comes out 0.51 or 1/2 molecule. Hence the original unit cube of KI with d = 3.532 has expanded to a very slightly distorted cube with an edge length of 4.68×10^{-8} cm and with an extra atom of iodine at or near the center.

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[1] J. Opt. Soc. America, 7, 472 (1923).

[2] [Nobody, not even Johnson, has ever claimed that KI_3 crystallizes first from such a solution.]

[3] [This cannot be true if KI_3 is a definite chemical compound.]

"Again, as in the case of KI, the spectrum of the reflection furnished striking configurations and additions. The KI_3 spectrum duplicates that of KI in that it is characteristic of iodine. The spectra of the former for the 100 and 010 planes show the iodine peaks at almost the same angles. A well-defined first-order peak at the top of the sharp absorption drop appears at 2°21′ and another, less prominent and incompletely separated, at 2°39′. As in the case of KI, the center of the absorption drop, the higher and the lower peaks have wave-lengths corresponding, respectively, to the critical absorption, the $K\beta$ and $K\alpha$ lines of iodine. The same reflections repeat themselves through 4 orders. Calculating *d* from $0.388 = 2\ d \sin (2°21')$ and $0.437 = 2\ d \sin (2°39')$ gives the value 470×10^{-8} cm. Considering that the calculation from a wave-length in the continuous spectrum involved an unusually long wave-length, 1.09Å, the value of *d* agrees remarkably well with that calculated from the characteristic iodine wave-lengths."

It is purely a grand-stand play to speak about studying solid potassium tri-iodide because of its importance in iodometric analysis. Solid potassium tri-iodide is not used in iodometry. It is important that iodine is soluble in a potassium iodide solution; but it is quite immaterial whether this is because of the formation of polyhalides or for some other reason.

There is nothing in this work of Clark and Duane to show that they had potassium tri-iodide at all. It all goes back to the now discredited analysis published by Johnson in 1877. Their own statements show that their material was impure. Pure iodine has a vapor pressure of 760 mm at 184.35° according to Ramsay and Young[1] and the dissociation pressure of a stable polyiodide cannot be higher than the vapor pressure of pure iodine. Clark and Duane claim that the dissociation pressure of the alleged compound is 760 mm at 146°, which is absurd, quite apart from the fact that we now know that there is no stable compound[2] between iodine and potassium iodide in contact with the melt. Clark and Duane's material must have contained water for it to have had the vapor pressure which they give. This is not surprising because we know from the melting-points that Johnson's preparations and those of Wells and Wheeler contained water. There does not seem to be any justification for mentioning a vapor pressure of 760 mm at 146° without comment, because Regnault had put the boiling-point of iodine at 175° as far back as 1862.

Clark and Duane did not determine the density of their material themselves but took the value found by Johnson which we know to be wrong because Johnson's material was not pure. Consequently Clark and Duane worked with impure material of unknown composition with a false density, and they calculated their results by means of a formula which did not apply. They resemble the billiard sharp in the Mikado, who played on a cloth untrue, with a twisted cue and elliptical billiard balls.

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[1] J. Chem. Soc., **49**, 461 (1886).

[2] Briggs: J. Phys. Chem., **34**, 2250 (1930).

We may seem to be a little harsh on Mr. Clark; but he has had over two years in which to correct the erroneous statement, made at Swampscott, that he had proved the existence of solid KI_3; and he has not taken advantage of the days of grace.

We are not the only people to criticize Mr. Clark's conclusions. R. W. G. Wyckoff[1] says that "both the data and their treatment are, however, incapable of proving anything definite about the manner of atomic arrangements in crystals with such low symmetry." Ewald and Hermann[2] say that "in these three papers [by Clark and Duane] they have worked with the selective reflection of the iodine radiation in KI_3 crystals. *The results are probably wrong.*"

Mr. H. M. Southworth of the Department of Physics at Cornell University was good enough to make some X-ray measurements by the powder method on potassium iodide and so-called potassium tri-iodide. The latter crystals were drained, ground, and put into tubes along with some adhering mother liquor.

Four spectrographs were made: two each from two tubes. The first pair were over-exposed; but the second, using exposures of 10 and 7 minutes respectively, were fairly good. In Table V are given the data read from the latter two films, with the lines for KI as computed for unit cell = 7.052Å[3] for a face-centered cube.[4]

TABLE V

n	KI comp.	I 10 min.		II 7 min.	
	7.052 Å/n½	KI	KI_3	KI	KI_3
3	4.07	4.07	4.07	4.05	4.05
4	3.53	3.49	3.49	3.49	3.49
8	2.49	2.50	2.50	2.48	2.48
11	2.12	2.12	2.12	2.12	2.12
12	2.04	2.04	2.04	2.03	2.03
16	1.76	1.76	1.76	1.76	1.76
19	1.62	1.62	1.62		
20	1.58	1.58	1.58		
24	1.440	1.443	1.443	1.44	1.44
27	1.358	1.358	1.358	1.355	
32	1.247	1.250			

"As is seen from the data, the lines observed check closely with the computed values, in the case of KI_3, as well as in that of KI. Except for the last line (n = 32), which was very faint for KI, lines were observed for KI_3

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[1] "The Structure of Crystals," 339 (1924).

[2] Strukturbericht, 287 (1913-1926).

[3] "International Critical Tables," 1, 345.

[4] Clark: "Applied X-rays," 134.

corresponding to each of the lines for KI, and no other lines for KI_3 were observed. The lines for KI_3 were in general fainter than those for KI."

We are not qualified to interpret X-ray data; but we are told that Table V is not an argument for the separate existence of KI_3. We express our sincerest thanks to Mr. Southworth.

The belief in the existence of a solid potassium tri-iodide, stable at 25°, rests on the analysis made by Johnson in 1877—which has since been shown to be wrong—and on the fact that a solid potassium tri-iodide was a natural thing to expect. In the paper already cited, Grinnell Jones says that he "gives greater weight to the definite, circumstantial, positive evidence of the existence of solid KI_3 than to the negative evidence of the investigators who failed to find it." As a general principle this is perfectly sound; but it happens to be an unfortunate position to take in this particular case.

We have duplicated Johnson's results and anybody can duplicate Johnson's results. In fact Wells and Wheeler did and Clark and Duane did. All three sets of people had material which was obviously impure from its properties, and Johnson was the only one who made an analysis. His analysis was made by a method which could not possibly give accurate results with such a substance as the hypothetical potassium tri-iodide. We have duplicated his analysis and have shown that the error was in the method and not in his manipulation. We have confirmed the experiments of Abegg and Hamburger and of Parsons and Whittemore that potassium tri-iodide does not crystallize from these solutions. A better statement by Grinnell Jones would have been that Johnson obtained KI_3 by an obviously inaccurate method of analysis, whereas Abegg and Hamburger and Parsons and Whittemore found no such compound, when using phase rule methods which are known to be more accurate. The analyses by Scherer confirm those by Parsons and Whittemore. As these last had been made before Grinnell Jones wrote his article, and as he had been told about them, one can hardly praise him for his calm, impartial attitude.

While the experiments with benzene by Abegg and Hamburger are puzzling and should be repeated, Parsons and Corliss[1] have obtained results with aqueous alcohol which agree absolutely with the later work by Parsons and Whittemore with water alone. From the view-point of phase-rule work, it is immaterial whether one uses pure water, pure alcohol, or any mixture of them as the solvent, provided the ratio of water to alcohol is kept constant throughout. If neither water nor alcohol forms part of the solid phases under the conditions of the experiment, the nature of the solid phases must be independent of the composition of the aqueous alcohol used.

"In order to obtain the solubility curves and corresponding solid phases for the system, various mixtures were prepared and placed in 100 cc. hard-glass bottles, the glass stoppers of which had been carefully ground. The bottles were then rotated in a large thermostat carefully regulated at 25°. The rotating was started December 1, 1909, and the bottles were removed from time to time for analysis and for the addition of more potassium iodide or of iodine as the case might require, should examination show that the solid phase had all disappeared. Equilibrium was reached most quickly in the more concentrated solutions, which was directly contrary to previous experience in pure alcohol. Many of the bottles had not reached equilibrium on March 1 after three months rotation. Practically all were in equilibrium by April 1; but the two where pure iodine alone was present in solution still showed slight gains on June 1 over analyses made some two weeks previously. They were, however, very near to saturation."

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[1] J. Am. Chem. Soc., 33, 1367 (1910).

TABLE VI

Solubility of Iodine and Potassium Iodide in Forty Percent Alcohol at 25°

Analysis of liquid phase			Analysis of solid phase with adhering mother liquor		
% KI	% I_2	% H_2O	% KI	% I_2	% H_2O
(a) In equilibrium with potassium iodide					
42.10	0.0	57.90	100.00	0.0	0.0
40.83	3.76	55.41	89.21	0.70	9.09
38.94	10.09	50.97	88.80	1.90	9.30
37.41	15.71	46.89	88.19	3.02	8.79
36.25	20.52	43.23	87.04	4.21	8.75
35.38	24.44	40.15	86.08	5.11	8.81
33.26	33.62	33.12	83.61	8.41	7.99
31.71	39.99	28.30	82.06	10.76	7.18
30.59	44.76	24.65	80.80	12.35	6.85
28.56	55.30	16.14	75.90	18.63	5.87
26.95	60.27	12.78	74.77	20.86	4.37
24.52	65.93	9.55	72.98	23.61	3.41
23.04	69.93	7.03	72.35	25.04	2.51
(b) In equilibrium with iodine					
0.0	2.97[1]	97.03	0.0	100.00	0.0
8.45	28.70	62.85	1.85	84.51	13.64
12.56	40.63	46.81	3.41	84.02	12.57
15.20	49.95	34.85	4.98	83.81	11.21
16.02	52.95	31.03	5.60	82.96	11.44
17.18	57.37	25.45	6.61	83.60	9.79
19.20	66.89	13.91	8.45	85.16	6.39
20.12	69.10	10.78	7.08	88.81	4.11
20.12	69.10	10.78	7.08	88.81	4.11
(c) Quadruple point					
22.50	70.79	6.71	19.48	76.24	4.28
22.43[2]	70.88	6.69	69.37	26.14	4.49

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[1] Final analysis June 1. Saturation may not have been quite reached.

[2] After addition of KI and further rotation.

The data for 40 percent alcohol are given in Table VI and Fig. 5; and those for 60 percent alcohol in Table VII and Fig. 6. In regard to Table VI Parsons and Corliss say: "The analyses given are the final ones after equilibrium had been proven. Their accuracy may be judged from seven analyses given of the most concentrated liquid at the invariant [quadruple] point No. 20. At this point the liquid was shown to be in equilibrium with iodine, with potassium iodide; and with two mixtures of iodine and potassium iodide. It was first found to be in equilibrium with two solid phases, which could from the nature of the curve be only iodine and potassium iodide. For the sake of further demonstration the liquid was separated from the solid, pure iodine added, and further rotated in the thermostat without change in composition. Potassium iodide was now added and it [the solution] was later found to be in equilibrium with this new mixture. It was again separated from the solid and rotated in contact with pure potassium iodide but no change in composition took place. As only two solid phases can co-exist at the invariant [quadruple] point, no polyiodide can be present. It might also be well to call attention to the highest concentration and the interesting fact that a mixture of twenty grams of potassium iodide and 72.5 grams of iodine can be kept in solution by 7.5 grams of 60 percent alcohol at 25°."

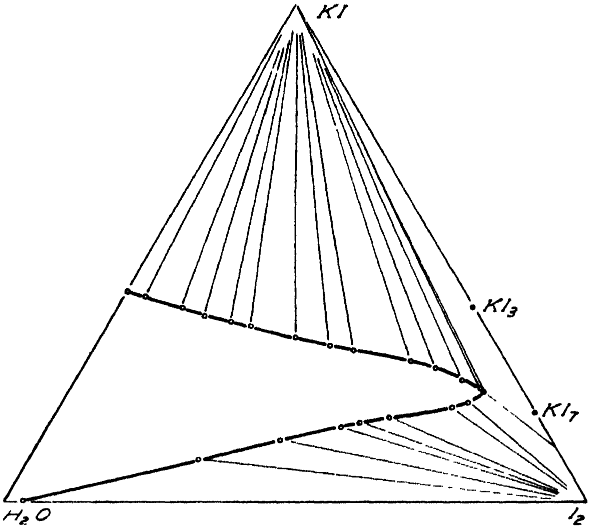

Fig. 5
Forty Percent Alcohol Isotherm at 25 degrees.

It is rather interesting to note what Parsons and Corliss[1] say about their predecessors in this field. "As usually happens, the literature contains claims for the existence of solid polyiodides of potassium and also evidence of the non-existence at least of the tri-iodide. Johnson[2] states that he succeeded in

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[1] J. Am. Chem. Soc., **33**, 1368 (1910).

[2] J. Chem. Soc., **31**, 249 (1877).

TABLE VII

Solubility of Iodine and Potassium Iodide in Sixty Percent Alcohol at 25°

Analysis of liquid phase			Analysis of solid phase with adhering mother liquor		
% KI	% I_2	% H_2O	% KI	% I_2	% H_2O
(a) In equilibrium with potassium iodide					
30.93	0.0	69.07	100.00	0.0	0.0
29.87	4.51	65.69	89.13	0.71	10.16
28.39	12.48	59.13	86.60	2.27	11.13
28.00	18.60	53.40	87.30	3.21	9.49
27.60	21.80	50.60	85.75	4.25	10.00
27.00	28.00	45.00	84.39	6.05	9.56
25.90	40.52	33.58	81.05	10.30	8.65
24.90	52.42	22.68	76.21	16.73	7.06
24.40	58.93	17.67	73.20	21.04	5.76
22.49	65.75	11.76	71.66	24.15	4.19
21.50	68.95	9.55	70.04	26.42	3.54
(b) In equilibrium with iodine					
0.0	23.04[1]	76.96	0.0	100.00	0.0
7.36	43.05	49.59	1.40	88.76	9.84
10.60	49.38	40.02	2.50	88.21	9.29
12.44	55.33	32.23	3.72	87.10	9.18
13.74	59.26	27.00	4.41	86.60	8.99
15.20	62.66	22.14	5.80	85.20	9.00
17.72	69.10	13.18	7.15	85.49	7.36
19.30	71.90	8.80	7.45	88.96	4.59
(c) Quadruple point					
20.11[2]	72.51	7.38	—	—	—
20.03	72.46	7.51	21.84	74.64	3.52
20.05	72.54	7.41	—	—	—
19.98	72.44	7.58	7.40	89.81	2.79
20.08	72.51	7.41	20.61	74.09	5.30
20.06	72.44	7.50	—	—	—
20.05	72.48	7.47	33.46	63.19	3.35

obtaining lustrous, dark-blue crystals by evaporating concentrated solutions of iodine in both aqueous and alcoholic potassium iodide, which analysis showed him to be the tri-iodide. As all the mixed crystals obtained from these strong solutions have much the same appearance and can not be separated from the mother liquor, his conclusions are not to be relied upon, especially as analysis is no criterion whatever of the formula of a substance unless its identity as a single compound is proven by other means. The more recent work of Abegg and Hamburger[1] upon solutions of iodine in aqueous potassium iodide is extensive, and they conclude that no polyiodide of potassium exists of less complexity than KI_7. A difference of opinion may be held as to whether the solid phase they analyzed as near to KI_7 was in reality homogeneous. Foote and Chalker[2] give results which, if correct, prove the existence of KI_3 and KI_7. They are in direct opposition to our own and both cannot be right. We must leave the judgment to others. We can only suggest that possibly equilibrium was not attained, that the analyses of the solutions supposed to be constant are not in sufficient agreement to prove constancy of composition and that in these concentrated solutions the potassium iodide content of the solid phase, after pressing between filter paper, is alone no real criterion of its true composition. Furthermore, we are unable to plot their results on any semblance to a solubility curve."

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[1] Final analysis June 1, saturation point may not have been quite reached.

[2] Analysis April 12.

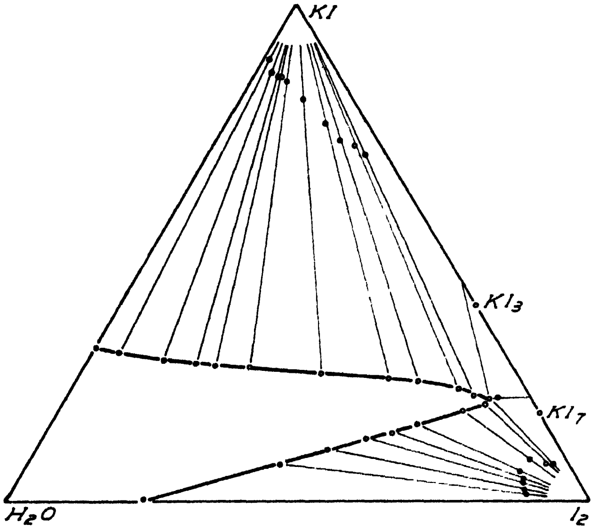

FIG. 6
Sixty Percent Alcohol Isotherm at 25 degrees.

It is difficult to believe that Grinnell Jones read the papers by Parsons and Corliss, and Parsons and Whittemore either sympathetically or understandingly. He has quite overlooked what everybody knows, that the man who challenges the work of his predecessors has usually taken some pains to satisfy himself that his work is right. He should receive at least as much consideration as the man who never knew that anybody was going to question his data. It is quite certain that Foote and Chalker would have taken more pains if it had occurred to them that their data would be challenged. Most people would also have noted that nobody has attempted to controvert the data published by Parsons more than twenty years ago.

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[1] Z. anorg. Chem., 31, 249 (1906).

[2] Am. Chem. J., 39, 561 (1908).

The fact is that the only evidence for the existence of solid potassium tri-iodide is the analysis by Johnson in 1877 of an admittedly impure product by an admittedly inaccurate method. The experiments of Wells and Wheeler were made with an impure product—as shown by the melting-point—which they did not analyze. There is nothing in their results inconsistent with the assumption that their product was essentially potassium iodide which had taken up enough iodine to change one of the axes slightly. Clark and Duane worked with an impure product—as shown by the boiling-point—which they did not analyze. There is nothing in their results inconsistent with the assumption that their product was essentially potassium iodide which had taken up enough iodine to change one of the axes slightly. The phase rule studies by Abegg and Hamburger, Foote and Chalker, Parsons and Whittemore, and Scherer show no signs of potassium tri-iodide as a solid phase at 25°, while Briggs has shown that no polyiodide exists in stable equilibrium with the melt. The evidence against the existence of potassium tri-iodide as a solid phase stable at 25° is overwhelming. On the other side there is one inaccurate set of analyses, made before any doubt had been cast on the existence of solid potassium tri-iodide. The work of Parsons and Corliss with aqueous alcohol confirms the results of Parsons and Whittemore. The work of Abegg and Hamburger with benzene appears to prove the existence of solid KI_7.

The general results of this paper are as follows:—

1. In 1877 Johnson analyzed impure crystals from a potassium iodide-iodine solution and seemed to prove that the solid phase was KI_3. Johnson's experiments have been duplicated by Scherer who got the same results as Johnson; but who showed that these results were wrong.

2. Wells and Wheeler did not analyze their product but relied on Johnson's analysis which has now been discredited. The melting point of their product shows it to have been impure.

3. Clark and Duane did not analyze their product but relied on Johnson's analysis which has now been discredited. The boiling-point of their product shows it to have been impure.

4. Abegg and Hamburger, Foote and Chalker, and Parsons and Whittemore found no evidence of the existence of solid potassium tri-iodide at 25°. Their line of attack was sound theoretically, while Johnson's was not. It must be remembered that Johnson's method was the only one known at the time he did his experiments.

5. The experiments of Wells and Wheeler show nothing for or against the existence of solid potassium tri-iodide. Their results are consistent with the assumption that their product was potassium iodide which had taken up enough iodine to change one crystal axis slightly.

6. The experiments of Clark and Duane show nothing for or against the existence of solid potassium tri-iodide. Their results are consistent with the assumption that their product was potassium iodide which had taken up enough iodine to change one crystal axis slightly.

7. The X-ray measurements by Mr. H. M. Southworth of the Department of Physics show no signs of the presence of potassium tri-iodide.

8. The experiments of Briggs prove that no polyiodide of potassium can exist in stable equilibrium with the melt.

9. Our experiments prove that those of Parsons and Whittemore are not vitiated by presence of a metastable phase.

10. Solid potassium tri-iodide does not occur as a stable phase at 25°.

11. Parsons and Whittemore are right in saying that potassium iodide and iodine are the only solid phases which can be stable at 25°.

12. The experiments of Parsons and Corliss with aqueous alcohol confirm those of Parsons and Whittemore.

13. The experiments of Abegg and Hamburger appear to prove the existence of solid KI_7. Since this does not exist, there is something wrong about the experiments, possibly the assumption that iodine crystallizes pure from benzene.

14. Professor Grinnell Jones is right in saying that the non-existence of potassium tri-iodide as a solid phase stable at 25° proves nothing either way as to the existence or non-existence of potassium tri-iodide in solution. It is interesting, however, to note the lengths to which people have gone in trying to foster the belief that solid potassium tri-iodide does occur as a solid phase stable at 25°.

Cornell University.

THE REDUCTIVITY OF HYDROGEN AT CERTAIN METAL SURFACES IN RELATION TO THE OVERVOLTAGE[*]

BY G. RAYMOND HOOD[**] AND FRANCIS C. KRAUSKOPF

A study of the reduction effected by metallic couples such as Mg-Cu, Zn-Cu, in aqueous potassium chlorate solution and a comparison of the "reduction efficiency" of the hydrogen evolved in the several cases investigated[1] led us to inquire if some relation exists between the cathodic overvoltage and the efficiency of electrolytic reduction.

The correct method of determination of overvoltage is a disputed question. The proponents of the theory of transfer resistance uphold the commutator method of Newbery, which yields values independent of the density of the polarizing current.[2] Other investigators deny the existence of transfer resistance and support the direct method of measurement, which relates the overvoltage as a logarithmic function of the applied current.[3] From thermodynamical considerations, it is generally conceded that the latter method yields the more nearly correct results.[4]

Apparatus

An apparatus was constructed by which cathode potentials could be determined by the direct method during electrolytic reduction. This consisted essentially of (1) the electrolytic cell, (2) apparatus for the control and measurement of the electrolyzing current, (3) a reference electrode and potentiometer for the measurement of the cathode potential.

The electrolytic cell was a 400 c.c. beaker (Pyrex) equipped with motor-driven glass stirrer. The anode was a sheet of platinum foil, 2.5 × 1.25 × 0.02 cm., with a platinum lead sealed into a supporting glass tube containing mercury for electrical contact. The cathodes were in the form of rectangular plates, usually 2.0 × 4.0 cm., with an extension at one end, about 8.0 × 0.4 cm., which served as a support in fixing the cathode in position. In general, the back and edges of the cathode and the supporting strip were insulated so as to leave an area of 8.0 sq. cm. exposed, either with a coating of de Khotinsky cement covered with a film of paraffin wax, or with Vinylite 80.[1] In a few experiments where the cathode was uninsulated, the surface exposed to the electrolyte was 17 sq. cm. The electrodes were arranged with their plane faces parallel and opposite at a distance of 4 cm. and symmetrically with reference to the walls of the beaker.

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[*] Contribution from the laboratory of general chemistry of the University of Wisconsin.

[**] The material here presented is a portion of that used by G. Raymond Hood in his dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[1] W. Caldwell: Unpublished thesis, this laboratory (1928).

[2] Newbery: J. Chem. Soc., **105**, 2419 (1914); **109**, 1051, 1066, 1107, 1359 (1916); Sand, Weeks, and Worrell: **123**, 456, 1745 (1923).

[3] MacInnes: J. Am. Chem. Soc., **42**, 2233 (1920); Dunnill: J. Chem. Soc., **119**, 1081 (1921); Tartar and Keyes: J. Am. Chem. Soc., **44**, 557 (1922); Knobel, Caplan, and Eiseman: Trans. Am. Electrochem. Soc., **43**, 55 (1923); Glasstone: J. Chem. Soc., **123**, 2926 (1923); **125**, 2414 (1924); Knobel: J. Am. Chem. Soc., **46**, 2613 (1924).

[4] Jahn and Schoenrock: Z. physik. Chem., **16**, 53 (1895); Jahn: **26**, 422 (1898); Tafel: **50**, 641 (1905); Lewis and Jackson: **56**, 193 (1906).

The reference electrode was a saturated calomel half-cell of "Absolute" potential 0.472 volt at 20°C.; where the "Absolute" potential of the standard N/10 potassium chloride calomel cell is taken as 0.560 volt. The important feature of this part consisted of a double salt-bridge, where the liquid junction between the electrolyte and the saturated potassium chloride solution was made in a vessel outside the electrolytic cell, in order to prevent contamination of the cell contents, (Fig. 1.)

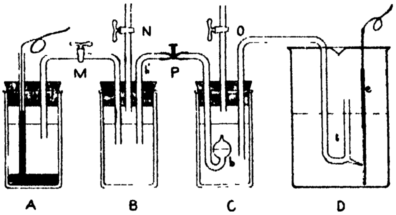

FIG. 1

A is the simple calomel half-cell, B a small jar of saturated KCl solution dyed with methylene blue, C is a similar jar containing the electrolyte used in the electrolytic vessel D. The construction of the tip t, which presses against the cathode face e, permits hydrogen entering it to pass freely to the surface. In setting up the apparatus, B was filled to a predetermined depth with fresh KCl solution, the clean dry jar C and the connecting tubing assembled, the part t dipping into the liquid in the beaker D. The cock M being closed, gentle air pressure at N forced KCl solution over until the bulb b was nearly but not quite filled. Closing N, and tightening the pinch-clamp P, the bulb could be filled until the KCl just entered the capillary. The open vertical tube of t was then closed with the tip of a finger and suction at O drew electrolyte into C until the level of the liquid in the jar was just below that of the electrolyte remaining in D; the final adjustment of the levels by siphonage proceeded until equilibrium was established. The cock O was then closed, the tip t was pressed against the face of the electrode, and all else made ready for the experiment. Then gentle pressure with the fingers forced out the small bubble of air trapped in the capillary of b, and opening the clamp P slowly drew electrolyte into b until the liquid junction rested at the widest portion of the bulb. Upon opening M the junction remained stationary at this desired position provided that pains were taken to insure the tightness of the rubber stoppers and the fit of the cocks M, N, O. The junction KCl—electrolyte obtained was beautifully sharp, and as the arrangement was not subjected to any movement after the junction was made it remained distinct for an hour or more. After the sharp definition of the junction became blurred, the rubber tube at P was compressed with the fingers until the bulb b was filled with KCl and overflowing—as could be seen by the streaky appearance of the heavier liquid falling through the electrolyte to the bottom of the jar C—careful release of the pressure drew back fresh electrolyte into b and a new distinct junction was formed. A slight closure of the clamp P brought the junction to the widest portion of the bulb.

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[1] A lacquer manufactured by the Carbide and Carbon Chemical Corporation, 30 East 42nd Street, New York City.

The drift in junction potential with this arrangement did not exceed 0.5 millivolt per hour; and potentials after renewal of the junction rarely varied by as much as 2 or 3 millivolts from those immediately preceding the renewal, and commonly agreed within a millivolt if the test electrode itself was in a consistently steady state. There is doubtless some fall in potential involved between the cathode and the half-cell element through the intervening double bridge, but this drop must be practically uniform among the several experiments. This apparatus effectually prevented contamination of the electrolyte; chloride neither diffused nor siphoned back into the electrolytic cell.

A variable resistance to adjust the applied current and an ammeter for its measurement—of 1.5 amperes range divided into 150 scale divisions—with a potentiometer for the determination of the E. M. F. of the cell: test electrode—calomel electrode, and the accessory wiring, completed the apparatus.

Experimental

Preliminary experiments with N/10 sulfuric acid as electrolyte showed that our overvoltage measurements exhibited marked imperfection from the quantitative standpoint. The observations were continued and the technique and experimental conditions checked by control tests until it was established to our satisfaction that the shortcomings in our data constituted a difficulty inherent in the problem and were not due primarily to faults in the apparatus or in manipulation.

The chief source of error, from the experimental side, lay in the variation in potential arising from slight differences in the position of the junction tip t with reference to the face of the test electrode and in the pressure with which it opposed the slight spring tension of the supporting strip, from one experiment to another. Our findings were quite in accord with those of other investigators;[1] the error attributable to these differences in the adjustment of the tip was not less than 5 millivolts, and at times may have amounted to 2 or 3 hundredths of a volt.

However, our results showed that the potential exhibited by a metal was influenced much more by its surface condition than by this or other factors (e.g., temperature, rate of stirring, etc.) which might affect it. The electrodes were polished uniformly with fine emery; but the surfaces could not be initially reproduced from one experiment to another.[2] Further, the process of electrolysis effected an alteration in the surface, so that the overvoltage varied markedly with time.[1] Thus in studying the relation between current density and overvoltage with nickel and copper cathodes, it was found that the order in which the observations were taken materially altered the results obtained. The theoretical relation

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[1] Knobel, Caplan, and Eiseman: Trans. Am. Electrochem. Soc., **43**, 55 (1923).

[2] Dunnill: J. Chem. Soc., **119**, 108 (1921); and others.

$$\pi = a + b.\log I$$

(where π is the overvoltage, I the polarizing current density, and a and b are constants)

which has been experimentally established in the case of mercury[2] and other metals, was not obtained when the current density was changed in a random manner; instead the relation was more nearly

$$\pi = a + b.I$$

contrary to the recent finding of Sand[3] with nickel and silver electrodes. The theoretical relation was approached if the observations were made methodically at continuously increasing current and at consistently longer time intervals. These discrepant results could only be attributed to alteration in the cathode surface resulting from electrolysis.

The cathode potentials of Cu, Al, Ni, Ag, Cd, and Fe in N/10 sulfuric acid as affected by time were studied in detail. In each experiment, the acid was electrolyzed at uniform current, usually for 5 hours—rarely for shorter intervals and occasionally for 10 hours—and the cathode potentials measured at intervals of from 3 to 30 minutes throughout this time. Individual points "off the curve" located by all the points seldom were in error by more than 3 to 5 millivolts at current density 0.0125 amp./sq. cm. The deviation increased slightly when the current was doubled.

The relation appeared to be specific for each metal, but for a given cathode the potential-time curves were fairly reproducible. Typical examples are given in Fig. 2, representing the potentials of iron and copper in N/10 sulfuric acid, at 0.0125 amp./sq. cm. The form of the curves for nickel at the same current density imitated those for copper, and the average maximum potential was identical with that attained by copper; i.e., 0.927 volt. The agreement among individual curves was however less satisfactory. The curves for silver started at a potential of 1.00 volt, and fell to a minimum of 0.84 volt in about 100 minutes, thereafter rising slowly; with closer agreement among the individual curves than was obtained with any other metal. Aluminum exhibited a sharp maximum potential; with wide variation among the several experiments. The average maximum potential was about 1.25 volt.

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[1] Beetz: Wied. Ann., **10**, 348 (1880); Roszkowski: Z. physik. Chem., **15**, 287 (1894); Förster and Piguet: Z. Elektrochemie, **10**, 718 (1904); Tafel (which see); and others.

[2] Bowden: Trans. Faraday Soc., **24**, 473 (1928); and others.

[3] Sand: Trans. Faraday Soc. **26**, 19 (1930).

The potential of copper was also measured at a number of current densities, determining a potential-time curve for each. The form of the curve at 0.0125 amp./sq. cm. was copied very exactly at higher currents to 0.0272 amp./sq. cm. but the individual error involved in failure to reproduce exactly the initial cathode surface obscured any quantitative relation between current density and the maximum potential. Certainly, the maximum π increased as I increased, but neither the relation

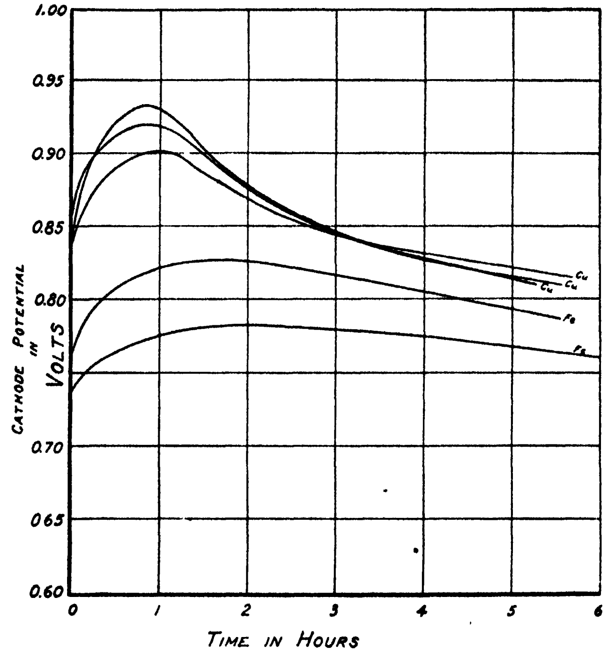

FIG. 2

$$\pi = a + b. \log I$$

nor

$$\pi = a + b. I$$

could be preferentially established from the observed values.

The apparent impossibility of obtaining closely reproducible potentials from one experiment to another and the variation in potential during the course of the electrolysis made it clear that in seeking a relation between overvoltage and reduction efficiency, the potential and the reduction must be concurrently determined.

Potassium chlorate was chosen as the reducible substance for this study: (1) because it affords an easy, accurate determination of the reduction accomplished (by gravimetric analysis for chloride) and (2) because the difficulty of the reduction would preclude marked changes in concentration which might obscure an existent relationship between the cathode potential and the current efficiency.

The chlorate was of technical quality (Merck), recrystallized 5 times. It then showed no trace of chloride. A solution was made up with redistilled water, approximately half-molar; the exact concentration was 0.493 Molal.

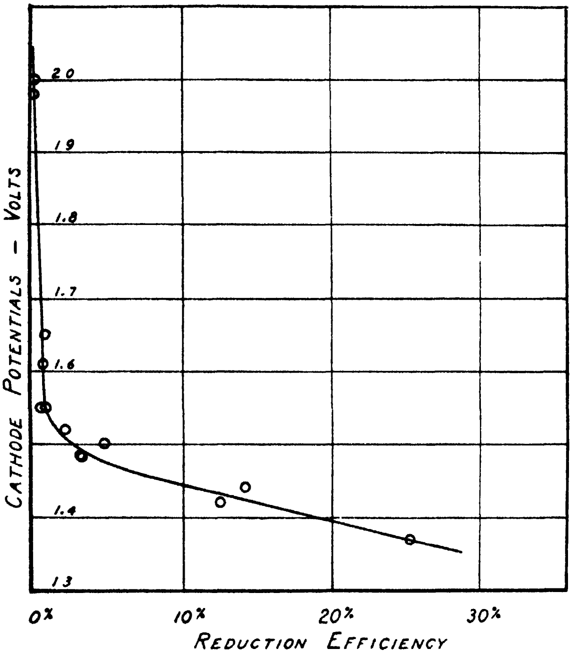

FIG. 3

Potential-time curves for Ag, Cu, Ni, Fe, Al, Sn, Zn, Cd, and Pt were observed over 5-hour periods during the electrolysis of (approximately) 200 c.c. portions of this solution under a uniform current of 0.30 amp. and the efficiency of the concurrent reduction was determined. In general, the potentials exhibited less variation with time in chlorate solution than in acid. The current efficiency was calculated on the basis of the equations

$$KClO_3 = KCl + 3\ O$$
$$Cl^{+++++} + 6\ e = Cl^-$$

One ampere-hour is then equivalent to 0.2204 g. of chloride. The chloride found, divided by 0.2204 g., equals the efficiency.

The results of these experiments are summarized in Table I and also presented graphically in Fig. 3. The cathode potentials are averages over 5 hours, and the reduction efficiencies found experimentally with cathodes of different areas are for easy comparison calculated to the corresponding efficiencies with a uniform area of 10 sq. cm.[1]

TABLE I

Cathode Metal	Current Density Amp./sq. cm.	Cathode Potential	Current Efficiency
Fe	0.0125	1.37	25.35%
Cu	0.025	1.42	12.55%
Fe	0.025	1.44	14.20%
Ag	0.0118	1.48	3.36%
Ag	0.025	1.485	3.23%
Cu*	0.0125*	1.50*	4.85%*
Ni	0.025	1.52	2.66%
Cu	0.0118	1.55	1.02%
Ni	0.0118	1.55	0.67%
Pt	0.032	1.61	0.78%
Cd	0.25	1.65	0.89%
Sn	0.0125	1.98	0.16%
Zn	0.0118	2.00	0.21%

* The polarizing current was 0.10 Amp. and 1/2 ampere-hour passed in this experiment.

The data show that when the potential of the cell: test electrode-calomel electrode exceeds 1.5 volt the electrolytic reduction is negligible, and that reduction occurs the more readily, the more the potential falls below this value.

Two other studies were carried out in an endeavor to throw some light upon the mechanism by which overvoltage occurs, and to correlate this mechanism with the process of reduction. The first of these consisted of a series of experiments on the catalytic reduction of potassium chlorate solution at room temperature by means of hydrogen in the presence of finely divided platinum.

Portions of platinum black were uniformly prepared by reduction of 1.0 gram samples of platinic chloride with magnesium powder and hydrochloric acid. Hydrogen gas, passing through a purification train of alkaline permanganate, alkaline pyrogallol, saturated mercuric chloride, and twice through redistilled water, was bubbled through measured volumes of well-stirred 0.493 M. $KClO_3$ in the presence of the catalyst for definite periods of from 4 to 28 hours, and the resulting chloride determined.

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[1] The data for aluminum are omitted from the table as a secondary phenomenon, i.e., solution of the cathode, intervened. In two experiments, apparent efficiencies of 53.78% and 77.21% were obtained at about 1.34 volt and 1.32 volt respectively. Corrected for the aluminum dissolved from the electrode, on the supposition that

$$2\ Al \rightleftharpoons Cl^-$$

these values were reduced to 21.42% and 26.25% resp. Cf. Lloyd: Trans. Faraday Soc., **26**, 15 (1930).

The reduction appeared to follow the law for unimolecular reaction processes.[1]

Another approach to the problem consisted of a study of decomposition potentials. These were measured by determining the break in the curve obtained by plotting the applied E. M. F. against the current.[2]

The anode was a square of bright platinum foil, 1 × 1 × 0.02 cm. with a platinum lead sealed into a supporting glass tube containing mercury for electrical contact. The platinum cathode was made identically; cathodes of other metals were formed from polished strips 1 cm. wide and of convenient length, insulated so as to leave 1 sq. cm. exposed. The decomposition potential curves for N/10 H_2SO_4, 0.493 M. KCl, and 0.493 M. $KClO_3$ were determined, using this platinum anode and cathodes of Pt, Cu, Fe, Ni, Al, Ag, and Sn arranged parallel and opposite at a distance of 4 mm. The observations were made according to a methodical, timed procedure, so that errors introduced by polarization phenomena at potentials above the decomposition potential were comparable among the several experiments.

The curves for platinum and iron given in Fig. 4 are typical of the results.

It was observed that the breaks in the decomposition curves for sulfuric acid occurred at increasing potential in the order of the metals: Pt, Fe, Ag, Cu (and Ni the same as Cu), and Al; in accord with the order of arrangement of increasing cathode potential in the same electrolyte. Likewise, the breaks in potassium chlorate agreed with the magnitude of the overvoltage: Fe, Cu and Ni, Ag, Pt, Sn—with Al in doubt.[3]

When the curves for potassium chloride were compared with those for chlorate for each cathode, another parallelism appeared. With a platinum

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[1] Saturation of the solution with hydrogen gas must have been accomplished in a relatively negligible time. The rate of formation of active hydrogen capable of effecting reduction from the ordinary inactive molecular form would therefore depend upon the superficial area of the platinum. The rate of reaction should depend upon the probability of collision between a molecule of the reducible body and the catalytic surface, and therefore upon its concentration alone.

The reductions obtained with different samples of catalyst were rather variable, and the reaction constant K obtained in a series of experiments with the same catalyst likewise varied to a considerable extent. The value of K increased quite irrespectively of the value of t in the formula

$$K = 1/t \,.\, \log \frac{a}{a - x}$$

but fairly steadily with the length of its use. Thus K at first increased about 1% per hour and later less rapidly for perhaps 60 hours, and then decreased, falling to about 2/3 of its initial value in another 40 hours.

This behavior was attributed to two causes: (1) that mechanical agitation in the course of a series of reduction experiments increased the area of the catalyst by breaking down clots of platinum black into smaller aggregates, enhancing the activity; and (2) that traces of impurity failing of removal from the hydrogen stream or introduced by successive additions of chlorate solution were adsorbed, depressing the activity. The initially preponderant dispersion phenomenon must approach a limit and the cumulative nature of the poisoning eventually decrease the reaction rate.

[2] Allmand: "Principles of Applied Electrochemistry," 112 (1920).

[3] The curve with aluminum really consisted of three parts: an initial portion of slop about 1.8 ma./volt; an intermediate slope of about 3.5 ma./volt beginning about 0.5 vol below the sharp break in the curve; and a final slope of about 230 ma./volt. The formation of $Al(OH)_3$ was observed over the intermediate portion of the curve, and solution of the electrode was rapid at higher E.M.Fs. If the second break marks the decomposition potential aluminum probably belongs between platinum and tin.

cathode, the curve for KCl broke at a lower potential than that for $KClO_3$, and so generally with the other metals. Iron proved an exception; and iron appeared to be the only metal capable of the reduction of chlorate with any marked degree of efficiency.

What appeared to be of more importance was that the difference in E. M. F.s between the decomposition potentials of H_2SO_4 and $KClO_3$ with the same cathode became progressively greater in the order of the metals: Fe, Cu and Ni, Pt, Sn. It was questionable whether silver should precede or follow platinum; and the position of aluminum was doubtful, but the order of magnitude of the increment of E. M. F. certainly placed this metal as more nearly allied to iron than to tin in its behavior.

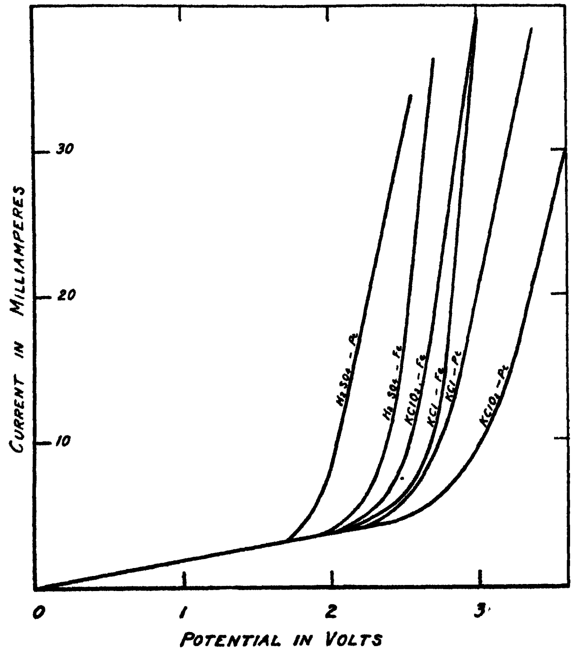

FIG. 4

Discussion

Of the various hypotheses which have been devised to explain what is taking place when an overvoltage occurs, the conception that the effect is due to the slowness with which monatomic hydrogen is converted into molecules seems most reasonable.[1] The theory supposes that metals of high overvoltage, possessing in a large degree the property of rendering difficult the escape of hydrogen gas from the cathode, will as a rule be capable of electrolytic reductions which are not produced by cathodes of lesser overvoltage.[2]

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[1] Tafel: Z. physik. Chem., **50**, 641 (1905); Lewis and Jackson: Proc. Am. Acad., **41**, 399 (1906); Bennett and Thompson: Trans. Am. Electrochem. Soc., **29**, 269 (1916).

[2] Tafel and Neumann: Z. physik. Chem., **50**, 713 (1905); Böhringer: Z. Elektrochemie, **12**, 745 (1906); Chilesotti: **12**, 146, 173, 197 (1906).

To explain anomalies, it has been suggested that other factors involved may mask the relation between hydrogen overvoltage and reducing power, e.g.: that one substance may be adsorbed at one cathode more easily than at another, so that the effective concentrations are changed, and conversely; that the electrode may act as a catalytic agent on the reaction; or that apparently inert substances in the electrolyte may modify the overvoltage.[1]

It does not appear to follow necessarily that a high concentration of monatomic hydrogen associated with large overvoltage implies a high reduction efficiency, save that it is the usual case. It was long since pointed out[2] that the activity of nascent hydrogen is intimately related to the nature of the reaction whence it originates, and it may be supposed that hydrogen *in statu nascendi* is monatomic hydrogen associated with a certain energy content varying with its mode of formation. That nascent hydrogen is the active agent in the reduction of chlorate seems evident from the experiments on catalytic reduction[3] while it appears from the decomposition potential measurements that the energy associated with the hydrogen atoms set free at the several electrodes must be greater in the order of the metals Fe, Cu and Ni, Ag?, Pt, Sn; i.e., in the order of the cathodes producing increasingly greater overvoltages and effecting less and less reduction in potassium chlorate solution.

The relative stability of hydrogen atoms in the gaseous phase lends weight to the hypothesis that their recombination into molecules involves a three-body collision.[4] If it is supposed that evolution of gas involves a comparable collision between hydrogen and hydrogen; and reduction a collision between hydrogen and chlorate at the cathode surface; the experimental facts appear to indicate that only *slow* or *cold* atoms can act as reductors. It has been noticed that close resonance is of importance for the transfer of energy among atoms and molecules involved in collision[5] in another field of study, and it is suggested that the application of the resonance principle is equally applicable in this connection.

Summary

An apparatus is described by which cathode potentials can be determined during electrolytic reduction without contamination of the electrolyte.

The efficiency of electrolytic reduction of aqueous potassium chlorate is negligible when the cathode potential exceeds 1.5 volt, and increases rapidly as the potential falls below this value.

Electrolytic reduction, catalytic reduction by hydrogen gas in the presence of platinum black, and decomposition potential measurements all point to the same conclusion as to the reaction mechanism.

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[1] Müller: Z. anorg. Chem., **26**, 1 (1901); Müller and Weber: Z. Elektrochemie, **9**, 955 (1903); Tafel and Emmert: Z. physik. Chem., **52**, 349 (1905).

[2] Tommasi: Chem. News, **40**, 245 (1879); **41**, 1, 176 (1880); J. Phys. Chem., **1**, 555 (1897).

[3] Hoitsema: Z. physik. Chem., 17, 1 (1895).

[4] Wood: Proc. Roy. Soc., **102A**, 1 (1922); Herzfeld: Z. Physik, **8**, 132 (1922).

[5] Cario and Franck: Z. Physik, **11**, 161 (1922); Beutler and Josephy: Naturwissenschaft, **15**, 540 (1927).

THE MECHANISM OF PLASTIC FLOW

BY G. E. CUNNINGHAM

The investigation discussed in this paper is an effort to arrive at some conclusion as to the fundamental difference or differences between the mechanisms of plastic and viscous flow, with particular reference to the plastic flow of clay pastes.

Most of the previous studies on the subject of plastic flow have been made by means of measurements of the rate of flow of the plastic material through capillaries of different dimensions and under different pressures. According to one theory,[1] the relation between the velocity of flow and the pressure is parabolic and may be expressed by the equation

$$V = k \cdot P^n$$

where k and n are constants for the given material. The Bingham theory[2] states that the velocity of flow is a linear function of the pressure and may be expressed by the equation

$$V = k(P - p)$$

where k and p are constants, p being the pressure required to start the flow, or the yield value. Unfortunately, neither of these theories is directly applicable unless the experimental data are obtained under "ideal" conditions.

The Bingham theory has proved useful in the study of slips and thin pastes, but it is well known that the deviation from the linear relationship not only is apparently much greater with some substances than others, but increases with the concentration of the solid phase in the mixture,[3] as one approaches the concentrations of the plastic state. Where experimental results have deviated but little from the ideal, corrections have been suggested to account for plug flow,[4] seepage and slippage,[5] proximity of a solid wall[6] and elastic deformation.[7] The deviation has also been attributed to a change in the consistency of the slip at high velocities of shear.

Schofield and Scott Blair[8] forced a clay paste through a metal tube which had a very small opening in the side for collecting a sample of material from the layer next the wall. No difference in the concentration of the paste was found, although quite an appreciable difference would have been required to account for the deviation from the linear relationship at low rates of shear.

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[1] cf. Ostwald et al: Kolloid-Z., **36**, 99, 157 (1925); **38**, 261 (1926); **43**, 190 (1927); **47**, 176 (1929).

[2] Bingham: "Fluidity and Plasticity," 217 (1922); Wilson: "Ceramics,—Clay Technology," 56 (1927).

[3] Cf. Green: Proc. Am. Soc. Testing Materials, **20** II, 451 (1920).

[4] Buckingham: Proc. Am. Soc. Testing Materials, **21**, 1154 (1921); Reiner: Kolloid-Z., **39**, 80 (1926); Scott Blair and Crowther: J. Phys. Chem., **33**, 321 (1929).

[5] Bingham: "Fluidity and Plasticity," 231 (1922).

[6] Scott Blair: J. Phys. Chem., **34**, 248, 1505 (1930).

[7] Bingham and Robertson: Kolloid-Z., **47**, 1 (1929).

[8] J. Phys. Chem., **34**, 259 (1930).

H. E. Phipps[1] determined the viscosity of cellulose acetate by both the capillary and the falling sphere types of viscosimeter, in the latter case using a series of spheres of the same size but different densities. Notwithstanding the marked difference between the methods, the curves were found to coincide over the curved portion at low shearing stresses.

Bingham[2] states that "polar" colloids exhibit the curvilinear relationship at low rates of shear, but "non-polar" colloids do not. However, clay was classed as a non-polar colloid and numerous examples may be cited (cf. Fig. 1) in which clay has exhibited the non-linear relationship. In another paper,[3] the same author states the theory, credited to F. Williamson, that the "apparent fluidity" of polar colloids is a linear function of the shearing stress.

It has been frequently recommended[4] that workers avoid difficulty by choosing the conditions of slip concentration, capillary dimensions and shearing force to ensure the linear relationship. This procedure, however, avoids the region of the curve which is different in shape from the curve for ideal liquids and the data fit the equation best when the measurements are made on the material when it is not in the plastic condition. Since the mobility (slope of the straight line) supposedly depends upon both the inherent plasticity and the dilution, which are independent of each other, it is difficult to know just what dilutions to use in order to compare the plasticities of two different substances.

Hall[5] attempted to solve this difficulty by making up the slips to the concentrations required to give equal mobilities, i. e., equal slopes of the pressure-velocity curves in the region of the linear relationship. He found that the more plastic of the two clays showed much the greater yield value. In each case, the relationship between velocity and pressure is far from linear and smooth curves may be drawn through the origin which include more of the experimental points than do the straight lines. In fact, the logarithm curves are better straight lines than the pressure-velocity curves, indicating the applicability in this case of the parabolic equation. For the purpose of the present discussion, however, it is sufficient to point out that the relation is not entirely linear. (See Fig. 1). The curves are approximately parallel in the upper portion, however, and Hall was perhaps justified in assuming that he had equal mobilities.

If we consider that the rate of flow is an actual measure of the fluidity (or mobility) at all pressures and that there is a change in the mobility with increasing pressure, we see that in the case of these two slips, of which the maximum mobilities are equal, the less plastic has the greater mobility at zero pressure and therefore the more plastic one undergoes the greater change in mobility before reaching the maximum.

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[1] Colloid Symposium Monograph, 5, 259 (1927).

[2] J. Phys. Chem., 29, 1201 (1925); Colloid Symposium Annual, 7, 207 (1930).

[3] Colloid Symposium Monograph, 5, 222 (1928).

[4] Bingham: Proc. Am. Soc. Testing Materials, 21, 1158, 1169 (1921); "Fluidity and Plasticity," 222 (1922).

[5] J. Am. Ceramic Soc., 5, 352 (1922).

Bleininger and Ross,[1] working with clay in the plastic condition, studied the relation between pressure and rate of flow through an orifice and found a curvilinear relationship. In apparent contradiction to the findings of Hall with thin slips, these workers found that, when each of the clays studied was made up to its maximum plasticity as judged by the working test, the pressure required to produce a given rate of flow was least with the most plastic clay and the others came in exact order of decreasing plasticity. These results seem to indicate that the more plastic the clay the less the pressure required to reduce its resistance to flow at a given value. Their investigation is considered of importance in this connection because their method duplicated the flow of clay through a die; and approximated the conditions of the potter's wheel more closely than does the flow of a slip through a capillary.

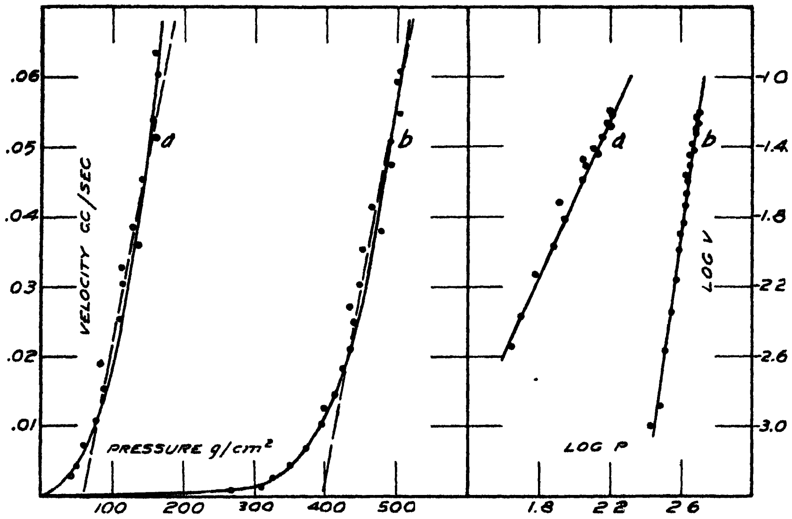

Fig. 1

Velocity of flow through a capillary.
(a) English China Clay, (b) English Ball Clay.
After Hall (loc. cit.)

If consideration be given to the possibility that plasticity is related to a change in viscosity with pressure, further consideration must be given to the possibility of, and reasons for, such a change.

It is common knowledge that pastes of clays and also of other materials "break down", or become fluid, with repeated working.[2] It is also well known among clay workers that a column of clay exuded through a die appears to be wetter than the same clay before pressing. J. W. Mellor[1] has shown that the amount of water required to wet a clay to maximum stickiness decreases with increasing pressure. For an earthenware body, the amount of water required was 26.4 per cent at atmospheric pressure and only 5.6 per cent at 200 kilograms per square centimeter. Hind[2] states that Mellor's data may be expressed by the equation

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[1] Trans. Am. Ceramic Soc., 16, 392 (1914).

[2] Cf. Hatschek: Kolloid-Z., 13, 88; Bergquist: J. Phys. Chem., 29, 1264 (1925).

$$A = 2.78 + 0.00437\ P^{3/2},$$

where A is the ratio of clay to water and P is the pressure in the above units.

On a basis of the above discussion, it does not seem unreasonable to assume that plasticity of a clay paste may be associated with a decrease in resistance to flow under the influence of pressure, caused by an increase in the actual liquid phase at the expense of adsorbed liquid or by a redistribution of the water in the gelatinous phase. If there were a coagulation of part of the gelatinous material in a clay paste under the influence of pressure, the water liberated would either remain between the particles of clay as free, lubricating, liquid or be taken up by the uncoagulated colloid, thereby producing a thinner gel.

Experimental

I. Relation of the Water Content of a Clay Paste to the Precipitating Centrifugal Force.

The water given up by the coagulated material is to be considered as at least momentarily free, as there is no other way to account for the phenomenon of seepage. In order to measure the quantity of water set free, seepage was purposely induced under varying pressures and the concentrations of the resulting pastes were determined. The following method of procedure was employed:

Approximately ten-gram samples of dry, pulverized clay were placed in weighed 30-cc. test tubes, the tubes then being filled to about two-thirds their depth with distilled water and shaken vigorously. After standing over night, the suspensions were shaken again and then centrifuged for thirty minutes at different speeds. The supernatant liquid was then poured off and the tubes were wiped dry, inside and out, and weighed. They were then dried to constant weight[3] at 125° C., and the ratio by weight of water to clay was calculated for each paste.

The rheostat by which the speed of the centrifuge was regulated was so designed that the setting of the dial was proportional to the centrifugal force, i. e., to the square of the angular velocity. The manufacturer's calibration was checked for the dial settings used and found to be correct. The diameter of the centrifuge at the tips of the tubes was 39 cm. and the maximum speed was about 3,000 r. p. m., giving a relative centrifugal force of about 2,000 times gravity.

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[1] Trans. Ceramic Soc. (England), **21**, 91 (1921-22).

[2] Trans. Ceramic Soc. (England), **29**, 177 (1930).

[3] In order to prevent the steam generated at the beginning of the heating from forcing the plug of clay out of the test tube, a weighed wick of rolled filter paper was forced to the bottom of the tube by means of a stiff wire. All weighings were made on a trip balance to the nearest 0.05 g.

The data obtained for the variation of the water content of several different clays with centrifugal force are given in Table I and plotted in Fig. 2.

TABLE I

Relation of the Water Content of Clay Pastes to Centrifugal Force

Rheostat setting	Ratio of water to clay				
	Experimental values				Average
	Florida kaolin				
5	1.250	1.226	1.231		1.24
10	0.900	0.830			0.87
15	0.735	0.770			0.75
20	0.715	0.740			0.73
	Kentucky ball clay				
5	0.974	1.000			0.99
10	0.815	0.785			0.80
15	0.645	0.715			0.68
20	0.654	0.644	0.667		0.65
	Scranton, Iowa, clay				
5	0.604	0.600			0.60
10	0.615	0.596			0.60
15	0.594	0.562			0.58
20	0.564	0.534			0.55
	North Carolina kaolin				
5	0.548	0.575	0.590	0.566	0.57
10	0.524	0.520	0.552	0.560	0.54
15	0.526	0.528	0.512	0.515	0.52
20	0.512	0.540	0.532	0.514	0.52
	Pulverized grog				
5	0.429	0.451			0.44
10	0.452	0.430			0.44
15	0.453	0.447			0.45
20	0.452	0.438			0.44
	Scranton, Iowa, clay + grog, 1:1				
5	0.568	0.590	0.606	0.597	0.59
10	0.531	0.544	0.569		0.55
15	0.438	0.465	0.491		0.46
20	0.421	0.444	0.504		0.45

It is interesting to observe that curve (e), Fig. 2, was obtained with a mixture of equal parts by weight of the materials used for curves (c) and (f), respectively. The curve for the mixture lies between the other two, but approaches the curve for the more plastic ingredient at low speeds and the other at high speeds.

The method was found to be inapplicable for clays of high colloid content (extremely "fat" clays) because the high centrifugal force necessary for complete precipitation did not leave a sufficient working range.

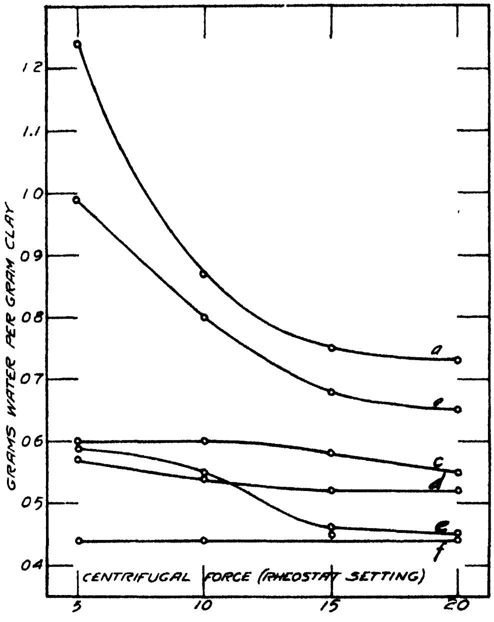

FIG. 2
Centrifugal force (rheostat setting)
Relation of water content of clay pastes to centrifugal force. (a) Florida kaolin; (b) Kentucky ball clay; (c) Scranton, Iowa, clay; (d) North Carolina kaolin; (e) Scranton, Iowa, clay + pulverized grog, 1:1; (f) pulverized grog.

It will be noted that some of the curves are concave upwards and others concave downwards, while one is an inflected curve showing bends in both directions and the non-plastic material, powdered grog, shows a constant water content. It is probable that, if one could work over a sufficient range of centrifugal forces, all the curves for the plastic materials would show the inflection. It is to be expected that if the pressure influences the extent of gelation at all, the effect occurs between two limiting pressure values.

II. Effect of External Pressure upon the Rate of Flow through a Funnel.

As a preliminary experiment, in order to ascertain whether pressure, independent of shearing force, exerted any effect upon the consistency of clay slip, a thick slip was poured into a Gooch funnel having a stem bore of about 7 mm. and the funnel was entirely enclosed in a vacuum desiccator. The lid was clamped on the desiccator and the time between drops of slip flowing through the funnel under its own head was determined in vacuo, at atmospheric pressure and at about three pounds per square inch above atmospheric pressure.

A marked decrease in the rate of flow was observed as the pressure decreased. During the first trial, however, bubbles of entrapped air expanded to considerable size in the stem of the funnel at low pressures and it was feared that they might be contributing to the retardation in the rate of flow. The experiment was therefore repeated with a slip which had been boiled to expel entrapped air, and the effect of a change in pressure was found to be even greater than before. As an extreme case, the time between drops was 4½ minutes in vacuo (water pump), 25 seconds at atmospheric pressure and 15 seconds at three pounds per square inch above atmospheric pressure.

III. Effect of External Pressure on the Mobility of Clay Pastes as determined in the Torsion Viscometer.

In order to make more accurate measurements of the effect of applied pressure on the mobility of clay pastes, the following apparatus was constructed:

A rectangular[1] box was made of sheet steel, of the correct dimensions to conveniently enclose a MacMichael torsion viscometer of the standard type. The viscometer was set permanently on the bottom, and the remainder of the box could be lifted away for filling and adjusting the viscometer, by means of a rope and pulley. When in place, the box was fastened to the bottom piece by means of bolts placed 1½ inches apart, the joint being sealed with a rubber gasket. The box was provided with an accurate pressure gauge and with stopcocks for the inlet and outlet of air. Electrical contacts for the viscometer motor and a 10-watt light were made through the bottom by means of brass screws passing through fibre washers. The speed-regulating screw on the gearing mechanism was turned to give the highest possible speed, and the speed of the motor was then regulated by means of a rheostat placed outside the box. A plate glass window in one side of the box facilitated observations of the angular velocity of the cup, and another in the top made it possible to read the angle of twist imparted to the wire.

The cup used had an inside diameter of 7 cm. and the plunger was a brass cylinder 1 cm. in diameter.

With stiff pastes, particularly of lean clays, it was not possible to center the plunger of the viscometer with sufficient accuracy to prevent some sidesway as the cup was rotated. This did not cause rotational oscillation in the torsion wire, but it caused the clay to work away from the plunger and the effect was increased at higher pressures. The difficulty was practically obviated by wrapping a single layer of sixteen-mesh copper gauze around the plunger. In order to prevent the paste from drying out during a series of observations, a beaker of water was placed inside the box to keep the air saturated with moisture.

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[1] For work at very high pressures, it would be desirable to have the box cylindrical in shape. This was not done in the present case because of the additional weight and volume entailed.

It will be seen that, with this method of procedure, the applied pressure is independent of the shearing force. Readings being made at a constant velocity of rotation, the rate of shear is kept constant; and the shearing force, measured by the twist in the wire, actually diminishes with decreasing resistance to shear.

Preliminary trials were made with moderately thick pastes, running the motor continuously and varying the pressure in steps of ten pounds per square inch. A marked decrease in the resistance to flow with increasing pressure was indicated but it was found impossible to obtain checks with a given sample. This difficulty was attributed to the probability that the effects of both the shearing force (local pressure) and the external pressure were not completely, or at least immediately, reversible.

Accordingly, the published data were obtained by making only one run with a given sample, checks being obtained by using another sample of the same composition. The pressure was increased in steps and readings were taken at a constant rate of shear at five-minute intervals until two consecutive equal readings were obtained, the motor being stopped between readings. The velocity of rotation was 10 to 20 r.p.m., depending upon the stiffness of the paste. The time for equilibrium was 45 minutes to 1 hour at 2½ pounds pressure, for the thickest pastes, decreasing to about 10 minutes at 40 pounds. The greater part of the change always took place within the first 5 to 10 minutes and equilibrium was reached much more quickly with thin pastes than with thick ones.

The thinnest of the pastes used were sufficiently thick to retain an unevenness in the surface over a period of several hours but were thin enough to pour, very slowly. The majority of them were thick enough to retain their shape indefinitely and the stiffest ones were not diluted much beyond the range of optimum workability, from the potter's point of view.

Each of the thinner pastes was made up by adding water to a previously unused portion of the thickest one. Each paste stood in a vacuum desiccator, which contained water instead of desiccating agent, for several hours before being used, for the purpose of removing entrapped air. There is, of course, the possibility that at high pressures air would redissolve in the paste and change the viscosity, but water so readily displaces adsorbed air from clay particles, and with the evolution of so much heat, that it is not likely that this source of error was very great. At most, it could account for only a small per cent of the observed effect of the pressure.

For the purpose of plotting, each of the mobilities at higher pressures was reduced to the fraction of the mobility at atmospheric pressure. In other words, the points plotted are reciprocals of the twist in the wire, the reading at atmospheric pressure being taken as unity. It is to be remembered that, while the initial readings are all given a value of one, the actual mobilities of the pastes increased with increasing dilution at all pressures. No effort was made to compare the mobilities of the different pastes quantitatively for the reasons that different wires, whose relative constants were not known, had to be used for different pastes, and it was not convenient to fill the cup to the same depth for each run, particularly with the stickier pastes. The wires used ranged from No. 17 Brown and Sharpe gauge piano wire to the No. 30 wire supplied by the manufacturers of the viscometer.

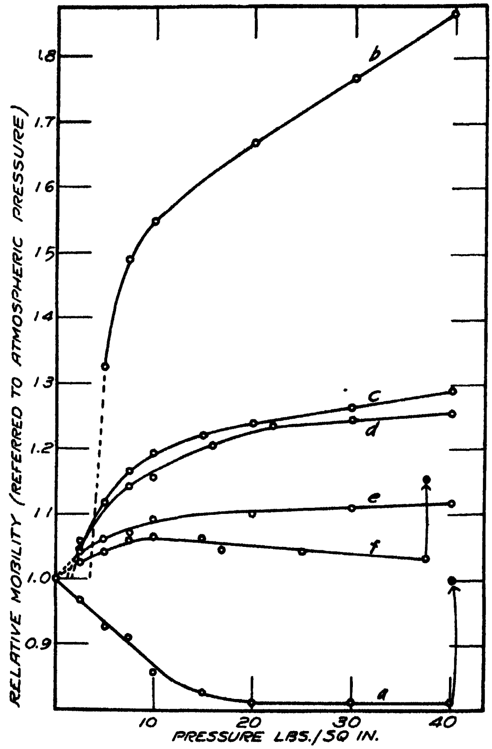

FIG. 3
Effect of pressure on the mobility of pastes of Kentucky ball clay; ratios of water to clay as follows: (a) 0.63; (b) 0.84; (c) 0.99; (d) 1.01; (e) 1.31; (f) 1.67. Solid circles: readings taken at atmospheric pressure immediately after pressures plotted.

Figs. 3 and 4 give the data obtained with pastes of Kentucky ball clay and North Carolina kaolin, respectively, pressures being plotted as abscissae and relative mobilities as ordinates. The ball clay is fat and plastic, while the kaolin is quite lean and possesses very little plasticity from the potter's point of view.

IV. Differential Effect of Pressure on Internal Friction.

The increase in the resistance to flow at low, and again at high, pressures may be attributed to a differential friction effect due to pressure before the increase in the liquid phase begins and again after it is complete. In Fig. 3, the points indicated by the solid circles are for readings taken at atmospheric pressure immediately following the reading at the pressure plotted. The inference was made that, while the differential friction effect is immediately reversed upon the removal of the applied pressure, the coagulation effect is not. Accordingly, runs were made in which the procedure was modified by following each differential pressure reading with a reading at atmospheric pressure, it being hoped in this way to trace the magnitude of each effect throughout the range of pressures studied. Fig. 5 shows the results of one

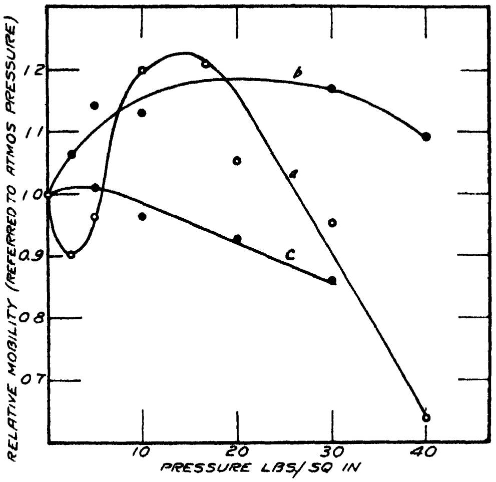

Fig. 4
Effect of pressures on the mobility of pastes of North Carolina kaolin; ratios of water to clay as follows: (a) 0.44; (b) 0.52; (c) 0.60.

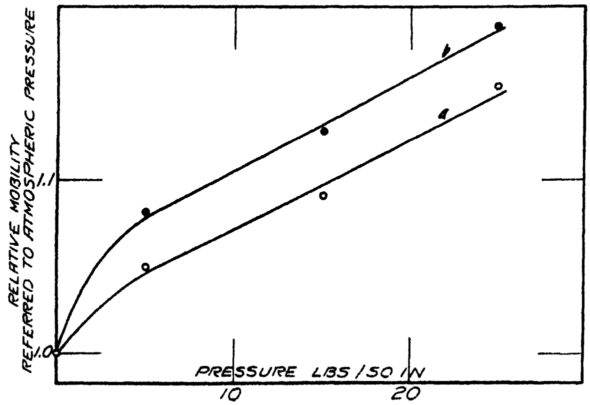

Fig. 5
Kentucky ball clay. (a) Values at pressures plotted; (b) values at atmospheric pressure immediately following pressures plotted.

such attempt with a very thin paste. The curve for the readings at atmospheric pressure falls above the curve for the readings at the increasing pressures. With thicker pastes, the experiment was unsuccessful, the atmospheric pressure curve coinciding with or even falling below the other. This is not to be interpreted as meaning that the differential friction effect was negative, which would be absurd, but rather that the reversibility of the liquid-gel change more than offset the decrease in internal friction when the pressure was released. The values at atmospheric pressure invariably decreased with time, and the readings therefore had to be taken as quickly as possible. Even in Fig. 5, the points on the upper curve probably are too low to give an exact indication of the magnitude of the friction effect.

Discussion of Results

It might, of course, be argued that the results of the experiments with the centrifuge do not prove the theory that water would be liberated under the influence of pressure in the absence of conditions which permitted seepage and consequent shrinkage in volume. However, they are exactly what one would expect if the theory were true. Moreover, there is no other obvious way to explain the decrease in the resistance to flow of the clay pastes when pressure was the only variable condition and seepage and breakdown of the gel structure due to shear were eliminated. (It will be recalled that the cup of the viscometer was not in motion except while readings were actually being made, and the recorded increases in the mobility took place between readings.) If there were simply a breakdown of gel structure due to contraction under pressure, the viscosity at a given pressure would be expected to increase with time as the gel had a chance to reset in its new position. There was no indication of the latter phenomenon.

Let it be assumed, therefore, that a symmetrical inflected curve is the ideal for the relation of free water content to pressure, any water which has been liberated being regarded as free water whether it has been taken up by other portions of the colloid or not, for the sake of convenience in the discussion. The P-W curve then takes the shape indicated in Fig. 6 (a), where P is the pressure and W is the content of free water. Plotting dW/dP against P then gives a curve of the shape of the theoretical probability curve as indicated in Fig. 6 (b). This is probably related to the quantity distribution of the increments of gel-forming material with regard to their swelling power. Conversely, of course, the amount of liquid phase present at any pressure is given by the area of the probability curve up to that pressure. Fig. 6 (b) was plotted by letting $c = 1$ in the theoretical equation[1]

$$dW/dP = \frac{c}{\sqrt{\pi}} e^{-c^2P^2},$$

and then translating the origin to avoid negative values of P.

If the mobility at any pressure p, as measured in the torsion viscometer, is to be compared with the mobility at atmospheric pressure, it must be remembered that the internal friction is greater when there is a high contact pressure between the particles than it would be for the same liquid content at atmospheric pressure. The rate of change of internal friction with pressure, dF/dP, will be constant as long as there is no appreciable change in the amount of free water present, i.e., at pressures less than p_1 and greater than p_2 in Fig. 6, and would be expected to have a smaller value in the latter pressure range than in the former on account of the higher content of free liquid in the paste. At pressures between p_1 and p_2, the value of dF/dP will be dependent upon the values of both W and dW/dP. Let W be the water content at pressure p, and ΔF and ΔW be the changes in friction and in free water, respectively, between the pressures of p and $(p + \Delta p)$. ΔF will be smaller the greater the value of W, and also will decrease with increasing values of ΔW. The value of ΔW might even become so great as to give ΔF a negative value. However, the total effect of the pressure on the friction must be positive at all points, so that the negative area between the P-dF/dP curve and the pressure axis, Fig. 6 (c), must never exceed the positive area.

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[1] E. B. Wilson: "Advanced Calculus," 388 (1912).

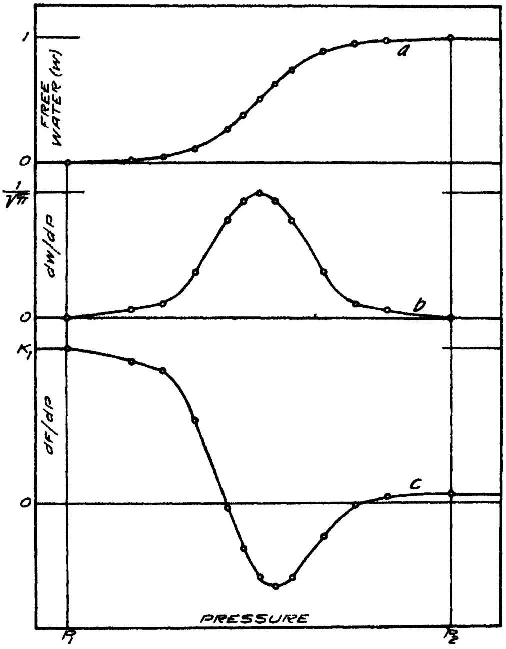

FIG. 6
Typical theoretical curves: (a) pressure-free water (P-W) curve; (b) P-dW/dP curve; (c) P-dF/dP curve (where F = internal friction).

These conditions are satisfied by the equation

$$dF/dP = k + f(dW/dP) + \Phi(W),$$

and for the purpose of plotting the theoretical curve it has been assumed that

$$dF/dP = k_1 - k_2 \cdot dW/dP - k_3 \cdot W.$$

Curve (c), Fig. 6, was plotted by assigning to the constants the relative values $k_1 : k_2 : k_3 = 1 : 1 : \frac{1}{2}$. Corresponding values of dW/dP and W were determined by estimating the area under the P-dW/dP curve, Fig. 6 (b).

It seems reasonable to assume that, neglecting the differential effect of pressure on the internal friction, the increase in mobility will be proportional to the increase in the amount of the lubricating liquid phase. On a basis of this assumption, the curve (M), Fig. 7, is obtained, in which the relative mobility referred to atmospheric pressure (neglecting friction) is plotted against pressure. The total increase in the mobility at any pressure is proportional to the corresponding area in Fig. 6 (b). The same curve could, of course, be obtained by direct reasoning from the P-W curve, Fig. 6 (a).

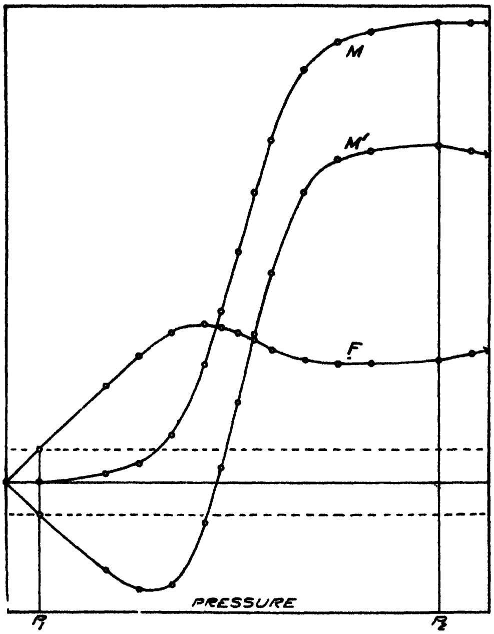

FIG. 7
Typical theoretical curves. (F) differential effect of pressure on internal friction; (M) effect of pressure on mobility, neglecting friction effect; (M′) effect of pressure on mobility, allowing for friction effect. (M′ = M − F).

The curve (F) in Fig. 7 shows the relation of the friction effect to the pressure. The value of the friction, F, at any pressure is given by the corresponding area under the P-dF/dP curve, Fig. 6 (c). A curve of the same general type could also be obtained by more direct reasoning: The relation between pressure and friction is linear in the regions where there is no change in the amount of liquid phase present, and the friction is less after the formation of free liquid has reached its limit than before it started. The two linear portions of the curve are joined by a smooth non-linear portion.

The net effect of the pressure upon the measured mobility is the difference between the two above mentioned effects, and gives a curve of the type M′, which is the difference between curves M and F.

The complete curve would be exhibited by a paste which contained no free water at the beginning, and in which the change was completed in the range of pressures studied. Curve (a), Fig. 4, is of this type. Curve (a), Fig. 3, is for a paste which contained no, or very little, free water at the beginning, but which did not give the complete change within the available increase of pressure.

Applying pressure has the same outward effect as increasing the water content of the paste, namely, that the degree of wetness is increased. It would be expected that those particles of clay, or better, perhaps, those incremental portions of gel which swell the least at atmospheric pressure would be the first to become saturated under the influence of increasing pressure. Therefore, regardless of whether the wetness is increased by adding water or by increasing the pressure, free water appears first in the same increments of gel. Therefore, if the paste contains free water at atmospheric pressure, the left-hand portion of the curves in Fig. 7 will disappear, the extent of the effect depending upon the amount of free water present. The effect of the free water formed as the result of the pressure will be relatively less, the greater the amount of free water already present. In other words, the integral effect of adding water to a clay paste is to cut off the left-hand portion of the P-M′ curve, and at the same time to expand the remaining portion of the curve in the direction of the pressure axis.

Curves (b), (c), (d), (e) and (f), Fig. 3, and (b) and (c), Fig. 4, give experimental justification of this portion of the theory. These curves, of course, approach the curve for pure water as the water content of the slip increases.[1]

The phenomena of flow through a capillary may also be explained on a basis of this theory. In a capillary viscometer, the bulk of the material is subjected to pressure within the bulb before entering the capillary. The material at the entrance to the capillary is under the applied pressure, but atmospheric pressure prevails at the exit. In other words, the flow is in the same direction as the application of pressure, so that the differential effect of the pressure on internal friction within the capillary itself is zero. For flow through a capillary, therefore, the mobility curve corresponds to the curve M in Fig. 7. It is seen that in its middle portion the curve is approximately linear, agreeing in this region with the theory of Williamson.[2] The velocity of flow, V, is proportional to both the mobility, M, and the pressure, P. Therefore,

$$V = C.M.P$$

where C is the proportionality constant arising from the constant factors in the Poiseuille equation. Since the effect of pressure is not instantaneous, there may be a time effect which would slightly alter the equation but would not influence the general shape of the curve. The greater portion of the material remains in the bulb under pressure for considerable time, and the pressure effect reaches its limit much more quickly with the thin pastes and slips such as have been almost universally used in the capillary type of viscometer than with the thicker pastes.

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[1] The viscosity of water also decreases under pressure, but at room temperature the decrease is only about one per cent for a pressure of 600 atmospheres. Cf. Bingham: "Fluidity and Plasticity," 139 (1922).

[2] loc. cit.

Fig. 8 shows two theoretical pressure-flow curves. Curve (a) was plotted by determining the value of P · M from the curve (M) in Fig. 7 and curve (b) was plotted from a similar P-M curve, not reproduced in this paper, obtained by substituting c = ½ in the probability equation for the relation of dW/dP to P. It is seen that in each case a curve is obtained which approximates the letter S in the lower portion, but which terminates at the upper end in a straight line (where M becomes constant) which may be extrapolated through the origin. The logarithm curves show that, neglecting the very lowest points, one parabolic relationship holds for the portion of the curve which is concave to the left and another for the portion which is concave to the right.

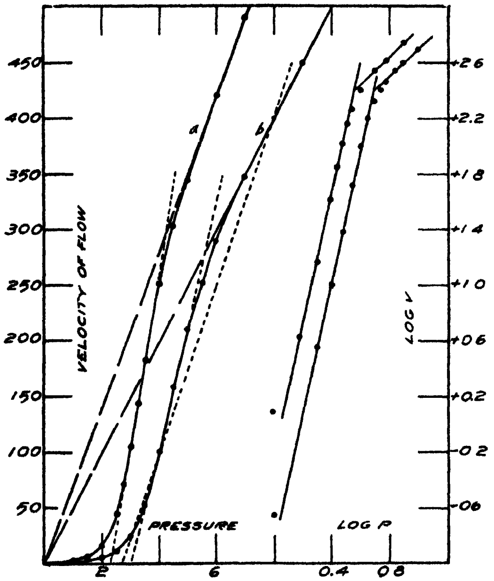

FIG. 8
Typical theoretical curves for flow through a capillary.

The dotted lines indicate other portions of the curve which might easily be taken as linear in an experimental determination of points provided the points were taken within too limited a range or too far apart. Particularly in the middle portion of the S is the approach to linearity quite close and this fact, together with the fact the relation is parabolic through this region as well as through the curved portion preceding it, makes it seem likely that it is the lower half of the S which has been the subject of controversy between the respective supporters of the parabolic and linear theories.

Two examples of data of other workers may be cited to illustrate the applicability of the theory. Curve (a), Fig. 9, was plotted from data obtained by Ostwald and Auerbach[1] using a one per cent gelatine solution and a burette type viscometer. The curve is exactly as those authors plotted it, except that approximately three-fourths of their points, all of which fall upon the curve within the limits of observation, are omitted. The curve has the exact shape of the theoretical curve except that in the extreme upper region there is a final curvature to the right. Ostwald assumes that the linear portion is the region of ideal flow, in which the material behaves as a true liquid. The S-curve is attributed by him to "structural" flow, that is, to the formation of clumps which are broken up by the consumption of energy from the shearing stress.[2] The curvature at the upper end of the straight line was attributed to turbulence in the liquid at high velocities of flow. Turbulence might well be given consideration, particularly with slips and thin pastes, but it is also

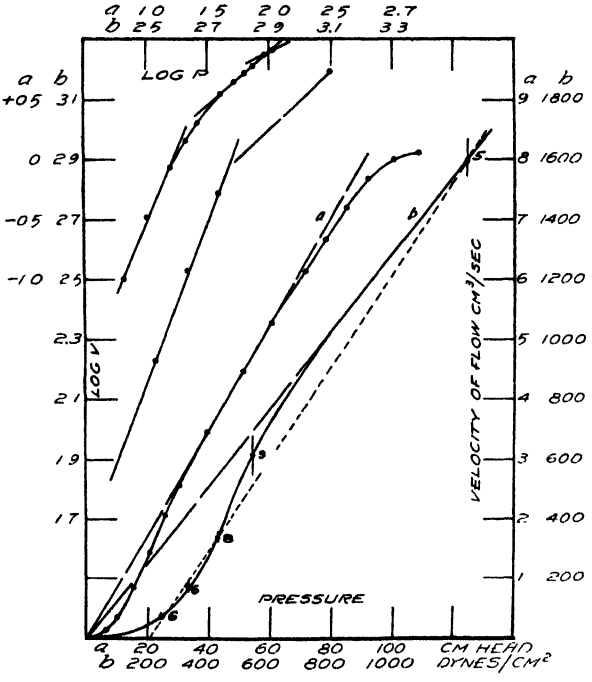

Fig. 9

Experimental curves for velocity of flow through a capillary. (a) One per cent gelatine solution, after Ostwald and Auerbach (loc. cit.); (b) 43 per cent ammonium oleate solution, from data of Bingham and Robertson (loc. cit.).

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[1] Kolloid-Z., 38, 261 (1926).

[2] cf. Bingham: Colloid Symposium Monograph, 2, 111 (1925).

true that the same effect would be produced if the rate at which the material could enter the capillary were retarded by the increase in the internal friction of the material in the bulb under high pressures, similar to the way in which sand may be held in a box which has relatively wide cracks in the bottom.

Curve (b), Fig. 9, was plotted from the data of Bingham and Robertson[1] obtained with a 43 per cent ammonium oleate solution. The short, vertical lines through the small circles include all the experimental values for the velocity of flow determined at the respective pressures, of which the points at the centers of the circles are the averages. The numbers beside the circles indicate the total number of accepted experimental determinations at each pressure. The dotted line is the line drawn by Bingham and Robertson in accordance with the Bingham theory. It passes through the averages of the third and fifth (counting upward) sets of points and entirely misses three sets of six, six and nine values, respectively. Moreover, neglecting the average values entirely, it is not possible to draw any straight line which even touches more than three of the five sets of points, except by taking the very lowest values in the fifth set, and that throws the fourth set still farther out of alignment. It seems that the nine values included in the fourth set of points are worthy of consideration for several reasons: The set contains more determinations than any other set of values; these values were determined at a higher rate of shear than the values in the three preceding sets and therefore, on a basis of the Bingham theory, should fall closer to the straight line than the preceding ones. It has been stated that a precision of 0.1 per cent is possible in fluidity determinations with the capillary viscometer,[2] and as the values under discussion have been further corrected for elastic deformation they should be at least moderately accurate.

It is seen that if a straight line be drawn which includes both the fourth and fifth groups of points, it leaves the other three groups on its right instead of on its left as would be expected on a basis of the Bingham theory. The logical conclusion in the absence of data for intermediate pressures therefore is that the curve is S shaped and, using the average values, would fall approximately as indicated by the solid line. This is borne out by the logarithm curve. It is not possible to determine from the data available whether or not there is a curvature to the right at the upper end of the straight line. With the thicker paste used in these experiments, turbulence would be less likely but the differential effect of the friction within the bulb would be more pronounced.

Time has not permitted a thorough search of the literature for additional data in agreement with the theory in the upper region of the curve, but it is believed to be safe to say that in the majority of cases where the supposedly linear relation has been followed through a considerable pressure range the upper points tend to veer either to the right or to the left of the straight line. They could shift either way, depending upon which portion of the theoretical curve was taken as linear.

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[1] Kolloid-Z., 47, 1 (1929).

[2] Bingham: Colloid Symposium Monograph, 2, 112 (1925).

It has been suggested to the author by Dr. E. E. Porter that probably the swelling process is a composite, rather than a simple, phenomenon; and that, while swelling as a whole is accompanied by a decrease in volume, there might be a particular contributory stage which causes or is related to the actual setting of the gel and which is accompanied by an increase in volume. If such were true, a reversal of the setting process would be favored by an increase in pressure.

If various stages of the composite effect took place simultaneously in different incremental portions of the gel, it would not be possible to detect an increase in volume due to one of the stages. It is not unlikely that an increase in pressure would increase the adsorptive power of certain portions of the colloid relative to other portions, with a consequent shifting of water from the latter portions to the former. This process might well be accompanied by a decrease in volume if there were a closer packing of molecules in the new arrangement.

The experiments seem to justify the conclusion that the property of plasticity is related to the ability of the plastic material to undergo a change in viscosity under the influence of pressure. The proposed theory precludes the possibility of a single substance's exhibiting the property of plasticity, but plasticity as outlined in this theory is not to be confused with the property of ductility, which may be regarded as the slippage of structural units, e.g., atomic planes in a crystal lattice or granules of solid held together by a fluid bonding agent. A plastic material is to be regarded as one of the latter type in which the bonding agent becomes more fluid under the influence of pressure.

A paste of clay which is quite lean, i.e., deficient of colloidal matter, does not afford conditions essential to a high degree of fluidity under any pressure. The flow of such a paste is to be regarded as more ductile than plastic in nature. On the other hand, a clay which is too fat, i.e., too rich in colloidal matter for optimum workability, produces a paste in which the bonding medium is quite fluid and causes trouble due to its stickiness. In such a paste the colloidal bonding phase is probably so uniform in structure that all portions of it are practically equally affected by a change in the pressure so that there is very little accompanying change in the mobility. Any possible change in the mobility is minimized in working the paste, due to the fact that the bonding medium flows so readily (when sufficiently wetted) that the shearing pressure is only momentarily applied to any portion of it. The addition of non-colloidal matter, such as grog, which frequently improves the plasticity of a fat clay, would be expected to influence the ability of colloidal matter clinging to its surface to adsorb water and thereby afford the proper conditions for a change in mobility under the influence of pressure.

A general outline of the above theory was drawn up after the data for curves (a) and (b) of Fig. 3 only had been obtained, and on a basis of the theory the general shape of each of the other curves was predicted accurately. In view of this, and of the fact that the existing data for flow through a capillary are also explained, it seems that, whether or not the theory gives a true picture of the mechanism of plastic flow, it is at least workable.

The theory of a change in the viscosity of gels caused by pressure should give a new turn to the problems of lubrication, since lubricating oils and greases are used under pressure. A study of the influence of pressure on the mobility of lubricating greases is now in progress.

The application of the theory to the comparison of various clays and other substances with regard to their plasticity is reserved for a later paper.

Acknowledgment

The original data published in this paper were secured by the author in the laboratories of Iowa State College.

Summary

On centrifuging clay suspensions at different velocities, a curvilinear relationship was found between water retained and centrifugal force, or pressure exerted on the gelatinous material. Plotting pressure against rate of change with respect to pressure of the amount of water retained gave a curve which corresponds to the theoretical probability curve.

In a viscometer, the free liquid which forms as the result of pressure on the gel remains between the particles and acts as a lubricant or forms a thinner gel.

Preliminary experiments showed that a clay slip flows through a funnel under its own head much more slowly in a partial vacuum than at higher pressures.

The effect of external pressure upon the mobility of clay pastes was studied quantitatively by means of a torsion viscometer entirely enclosed in a steel jacket in which the air pressure could be varied.

With thick pastes, the mobility was found to decrease at low pressures, increase far beyond its original value at intermediate pressures and decrease again at higher pressures. The net change at any given pressure was shown to be the difference between (1) the increase in mobility due to the increase of liquid water phase at the expense of adsorbed water and (2) the decrease due to the effect of increased pressure on the internal friction. Increasing the water content of the pastes tends to diminish both effects.

The theory has been shown to agree with existing data for flow through a capillary, and to correlate the Ostwald and Bingham theories.

The experiments seem to justify the conclusion that the property of plasticity is due to the ability of the plastic material to undergo a change in mobility under the influence of an applied pressure which may be entirely independent of the shearing force.

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DIELECTRIC CONSTANT AND STRUCTURE OF THIXOTROPIC SOLS*

BY S. S. KISTLER

Introduction

It has been found in recent years, particularly by Freundlich and co-workers,[1] that rather a large variety of colloidal solutions may under suitable circumstances display the property of thixotropy. This phenomenon has been subject to rather careful investigation. The conditions under which it may be caused to appear are fairly well known, accompanying optical phenomena have been subject to careful scrutiny, the relations between time of setting, temperature, size of vessel, and concentrations of sol and electrolyte are thoroughly cataloged (at least in the case of Fe_2O_3), and empirical rules devised; yet not very much positive evidence has been accumulated supporting any one theory of the cause of the phenomenon. Even well-formed theories are scarce. It was with the idea in mind that any light whatever shed on the subject would eventually contribute to the solution of the problem that the present work was undertaken.

That thixotropy in hydrophobic sols, such as those of Fe_2O_3, Al_2O_3, or V_2O_5, is closely connected with coagulation cannot be doubted. The same agencies which produce coagulation produce thixotropy. It seems that when the repelling forces between the colloidal particles are reduced to a certain point, reversible gelation may occur. If these forces are still further reduced, coagulation occurs.[2] The assembling of the particles into a semi-rigid framework, which, when disturbed, automatically reforms, has been explained by Haber[3] as being due to the "ionic cloud" surrounding the particles. Under suitable conditions of charge on the micelles and ionic concentration in the dispersing medium, the electrical forces are such that the micelles tend to assume fixed positions with respect to each other. If the gel is agitated, they assume the randomness of a sol; but, immediately upon the restoration of quiet, the orientating tendency exhibits itself again and gelation occurs. This conversion from sol to gel and vice-versa may be repeated an optional number of times without affect upon the cycle itself, unless the sol is sensitive to agitation and some disturbing effect arises such as coagulation.

On the other hand, numerous workers[4] have found the assumption of the existence of a hydration layer of considerable thickness surrounding the micelles, to be more satisfying. Upon approaching the conditions for thixotropy, the amount of water held more or less firmly by each particle in suspension increases until a point is reached where the particle no longer is free to move independently but becomes limited by its neighbors in such a way that the aggregate displays elastic resistance to deformation.

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* Contribution from the Kaiser Wilhelm Institut für physikalische Chemie und Elektrochemie, Berlin.

[1] H. Freundlich: Kolloid-Z., **46**, 289 (1928).

[2] W. Heller: Kolloid-Z., **50**, 125 (1930).

[3] F. Haber: J. Franklin Inst., **199**, 437 (1925).

[4] See for example E. A. Hauser: Kolloid-Z. **48**, 57 (1929); A. Paris: Sitzungsber. Naturforsch. Ges. Univ. Tartu, **35**, 135 (1929).

Evidence for the electrical hypothesis is to be found in the conditions necessary to bring about solidification in the hydrophobic sols. When electrolyte is added to the sol a little at a time, a point is finally reached where the solidification will occur if given enough time and if the sol is in a small enough vessel. Since one of the chief causes of precipitation in these sols is assumed to be electrical and since thixotropy has been shown to be so closely connected with precipitation, it is a small step to the assumption that the forces producing the gel are electrical in origin. The addition of non-electrolytes, such as alcohol, produces thixotropy.[5] This is attributed, however, to the increased "efficiency" of the electrolyte present, produced by the non-electrolyte. None of the hydrophobic sols are stable without the presence of some electrolyte.

In the case of Bentonite the transition from the thixotropic to non-thixotropic condition can readily be brought about by dialysis, and the thixotropic condition again induced by addition of electrolyte.

The affect of the individual ions also is such as would support the electrical hypothesis. The larger the charge of the anion the smaller the amount necessary to produce thixotropy. For example, Freundlich[1] lists the concentrations of various salts that have been found to have equal effects in inducing thixotropy in Fe_2O_3 sols as shown in Table I. The charge on the cation does not have so large an effect.

TABLE I

Electrolyte	Conc. Millimols/liter	Electrolyte	Conc. Millimols/liter
NaCl	45	Na_2SO_4	12
KCl	45	Na_2CrO_4	9.5
KBr	62	K_3Citrate	7
NaOH	18		

Heat is also effective, at least in the case of Fe_2O_3 sols, but here also it is not excluded that the primary effect is not on the concentration of the electrolyte or on the amount of electrolyte adsorbed.

On the other hand it has been assumed that the changes in electrolyte concentration effect changes in the amount of water held in the hydration shell surrounding the particles, and that the phenomenon of thixotropy is directly dependent upon hydration, which itself is dependent upon electrolyte concentration.

Very strong evidence limiting the applicability of the purely electrical hypothesis is to be found in the existence of thixotropy in hydrophilic sols such as gelatin[6] that are very insensitive to changes in electrolyte concentration, and in other sols where the presence of foreign electrolyte is entirely unnecessary, such as those of barium malonate and dibenzoylcystine.[7]

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[5] E. Schalek and A. Szigvari: Kolloid-Z., **33**, 326 (1923).

[6] Freundlich and Abramson: Z. physik. Chem., **131**, 278 (1927).

That aggregation of the particles of a sol does not accompany the production of thixotropy was well shown by Hauser in the case of Bentonite sols.[8] He observed dialyzed Bentonite sols under the ultramicroscope while the electrolyte concentration was gradually increased. A small addition stops the translatory Brownian movement, while a little more stops also the rotatory movement. An excess of the salt produces coagulation, but with the concentrations to be found in the thixotropic gels the evidence is that the particles are no closer together than in the sols. Hauser considers that an increased hydration layer due to the presence of the salt accounts for the observed phenomena.

General Considerations

According to the Debye theory of the origin of dielectric constant in polar substances, it can readily be shown that an adsorbed layer should have a different and in general a lower dielectric constant than the free substance. It is well known that the measurements of dielectric constants in vapors and gases of large molecular weight are attended with difficulties on account of the adsorption on the electrodes with the consequent uncertainty in both the actual mass of gas between the electrodes and the dielectric constant of the adsorbed part. Palmer[9] finds that it is necessary to assume a dielectric constant of approximately 3.5 for adsorbed water vapor on fine tungsten wire in order to explain his experiments on contact resistance.

Kallmann and Dorsch[10] carried out some very fine measurements on the dielectric constants of thin films of liquids in an attempt to find an effect due to the adsorption or orientation of molecules on the electrodes, but in spite of the accuracy attained were not able to demonstrate any effect. Unfortunately, the number of molecules whose dielectric constants must be changed by proximity to the electrodes in order to give a measurable effect by this method is so large that a negative result is rather to be expected than to be surprising. Indeed, it would be astonishing if the sought effect were large enough to be so measured.

Marinesco[11] has been active in determining the degree of hydration of hydrophilic colloids by measurement of their dielectric constants at 6.5 meters wave-length. He has assumed that surrounding every particle of the disperse phase there is a layer of water that has been "dielectrically saturated." For example, he calculates the thickness of the water envelope surrounding a methemoglobin particle of radius 27×10^{-8} cm. to be 70×10^{-8} cm. He arrives at the conclusion that crystalline hemoglobin "fixes" 15 grams of water per gram of hemoglobin, gelatin 8-10 grams and egg albumin 11-13 grams. By introducing degree of hydration he is able to calculate the dielectric constants of levulose solutions with fair agreement with the measurements.

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[7] H. Zocher and W. Albu: Kolloid-Z., **46**, 27 (1928).

[8] E. A. Hauser: Kolloid-Z., **48**, 57 (1929).

[9] W. G. Palmer: Proc. Roy. Soc., **106A**, 55 (1924).

[10] H. Kallmann and K. E. Dorsch: Z. physik. Chem., **126**, 305 (1927).

[11] N. Marinesco: Compt. rend., **189**, 1274 (1929).

Although such calculations are undoubtedly of high value in indicating the direction in which to look in a search for a measure of the amount of hydration of colloidal particles, the assumptions made are perhaps a little too simple. If a shell of water is "fixed" around each particle so that it displays only the dielectric constant of ice, the mechanism of this fixation should at least be placed on a plausible basis. Electrical saturation effects undoubtedly occur in solutions of electrolytes, where the field strength surrounding an ion is large. Sack[12] has calculated the sphere of influence of an ion and arrived at the conclusion that the influence of the ion is practically independent of its radius and may be expressed by the equation

$$\epsilon^* = \epsilon\,(1-\gamma C)$$

where ϵ^* is the observed dielectric constant of a solution, ϵ is the actual dielectric constant, C is the concentration in moles per liter and γ is a constant for any one salt and varies from salt to salt directly with the number of ions produced and as the 3/2 power of the valences of the ions. In the case of a colloidal solution, the concentration C is so small that even though there are numerous charges per micelle and the effect of the radius is included, the total measurable effect of the electric saturation on the dielectric constant is negligible unless γ is of an entirely different order of magnitude than that found for electrolytes. The existence of a field of 70 Å thickness surrounding a hemoglobin particle so strong as to greatly change the apparent dielectric constant of the water molecules within it through electric saturation is certainly not to be expected.

On the other hand, it seems reasonable to assume that while the field does produce electrical saturation in a few molecules closest to the micelle it also has an effect upon the freedom of rotation of the molecules much farther removed, due to the orientation produced and their tendency to link up into chains.[13] This linking tendency with its consequent interference with the freedom of rotation would presumably be most intense near the micelle and decrease with distance from it. It would be observed as an increased relaxation time for the molecules affected. This predicted increased relaxation time would tend to give abnormally low dielectric constants, just as has been found to be the case with the solutions studied by Marinesco.

The amount of this reduction of the measured dielectric constant will depend upon the frequency used in making the measurements, and it no longer is possible to make a simple calculation of the degree of hydration from measurements at one wave-length without the introduction of an arbitrary definition.

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[12] H. Sack: Physik. Z., 27, 206 (1926).

[13] J. W. McBain, [Nature, 120, 362 (1927)], considers the tendency of molecules to orientate at a surface and for transient chains to form extending from the orientated layer considerable distances, to be a very general tendency in liquids.

The fact that values of the dielectric constant of non-conducting solutions may vary with wave-length has often been neglected. It is well illustrated by measurements on sucrose.

Table II and Fig. 1 show the measured values obtained by Harrington[14] with a wave-length of approximately 300 meters, the author at 140 meters, Keller[15] at 76 cm. and the author at 32.7 cm.

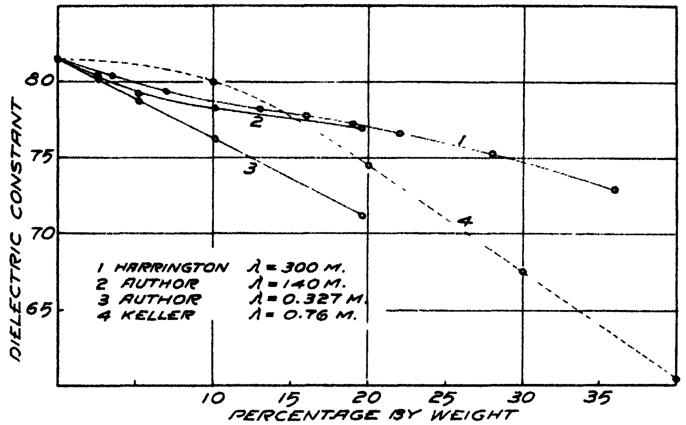

FIG. 1
Sucrose Solutions

TABLE II
Dielectric Constants of Sucrose Solutions

Harrington*		Author			Keller*	
300 m.		140 m.		32.7 cm.	76 cm.	
% wt.	D. C.	% wt.	D. C.	D. C.	%wt.	D. C.
0.0	81.5	0.0	81.5	81.5	0.0	81.5
3.5	80.4	2.6	80.5	80.2	10.	80.0
7.	79.4	5.15	79.3	78.7	20.	74.5
13.	78.2	10.10	78.3	76.2	30.	67.5
16.	77.7	19.45	77.0	71.1	40.	60.4
19.	77.2				50.	49.3
22.	76.5					
28.	75.1					
36.	72.9					
41.	71.1					

* Recalculated to a fiducial value for water of 81.5.

The figure illustrates well the necessity of taking the wave-length into consideration in any theory devised to explain the slope of the solute concentration-dielectric constant curve. (It seems evident that the data of Keller's are not to be relied upon.)

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[14] E. A. Harrington: Phys. Rev., (2) 8, 581 (1916).
[15] R. Keller: Kolloid-Z., 29, 193 (1921).

One might adopt as the degree of hydration that which is measured with such low frequency oscillations that only molecules very strongly bound will fail to rotate freely, but from the work of Kitchen and Mueller[16] on rosin and that of Errera[17] on ice, it appears that even molecules that might be thought of as being solidified on a surface, will have measurable relaxation times, and therefore a constant value for hydration at long wave-lengths is not to be looked for.

The function connecting the increase in the relaxation time of the solvent molecules with distance from the particle surface is entirely unknown; but one can safely assume that the effect decreases rapidly with distance, so that only molecules lying comparatively close are greatly affected. The nature of the function can be found by a study of the variation with varying frequency attributable to the solute of the dielectric constant. The nearer the frequency used lies to the frequency at which the uninfluenced solvent molecules no longer can freely follow the alternations in polarity of the field, the greater will be the influence of the solute on the measured dielectric constant. The greatest influence will occur where the curve connecting dielectric constant with frequency has a maximum slope. The lower limit of frequency available for studying solvation is probably in the region where the large molecule or particle, if polar, begins to follow the changes in the field and thus exhibits its own polarity. If the calculation of the degree of solvation is based upon measurements at one frequency only, one automatically introduces an arbitrariness into the results. Such results may have good value for comparison between several substances if the same wave-length is used throughout.

The earlier objection to the electric field surrounding a hemoglobin particle extending for 70 Å from the surface with such intensity as to produce electrical saturation applies also to some extent to the present argument. Rather than think of a hydrophile micelle as being surrounded by such a mass of strongly influenced water molecules, it is perhaps better to think of the particle as containing much water within its structure in such a way that very many molecules of water can come within a strong field of influence. In fact, that can well explain the fact that it has been difficult to demonstrate any hydration of hydrophobe colloids. The particles are compact and therefore a relatively much smaller mass of water is influenced.

If there is a sufficiently large sphere of influenced water surrounding the hydrophobe particles in a thixotropic gel, such as that of Fe_2O_3, to account for the solid condition, it should have a measurably smaller dielectric constant at very high frequencies than that of pure water. The present work is an attempt to measure this change in dielectric constant as a sol is brought to the thixotropic condition and then as it is allowed to solidify.

Kallmann and Kreidl[18] investigated the dielectric constant of V_2O_5 sols and thixotropic gels at a wave-length of 50 m. and found that while that of the gel was the same as that of water the sol had a dielectric constant of about 6% higher. No conclusions can be drawn from these results concerning the hydration of the particles or the condition of the water between the micelles in the gel except that the water is not solidified. The larger dielectric constant of the sol was undoubtedly due to some orientation of the smaller particles in the oscillating field, while this was prevented in the gel. In radio parlance a wave-length of 50 m. is considered very short, but it is still so far from the anomalous dispersion region for water that only very large changes in relaxation time of the molecules could be detected.

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[16] D. W. Kitchen and Hans Mueller: Phys. Rev., (2) **32**, 979 (1928).
[17] J. Errera: J. Phys., (6) **5**, 304 (1925).
[18] Not yet published.

In addition to the necessity for working at very high frequency, it has the very real advantage of eliminating the disturbing influence of small quantities of electrolyte. On the other hand, accurate measurement of dielectric constant with wave-lengths less than a meter becomes difficult due to the necessity of using one of the Drude methods[19] involving standing waves on parallel wires or an optical method such as that of Nichols and Tear.[20] Of greatest difficulty is the generation of undamped oscillations sufficiently rapid, intense and constant.[21]

The most ideal wave-length with which to work with these sols would be less than 10 cm. but due to the difficulties involved it was decided to work with somewhat longer wave-lengths at first and eventually carry the measurements to this frequency. Owing to the constancy of wave-length and the satisfactory intensity obtained, it was decided to use the special high frequency tube modeled after the directions of Kohl[22] made by the Telefon-, Apparat-, Kabel-, und Drahtwerke A. G., Nuernberg, Germany. The wave-length obtained was 32.7 cm. and remained very satisfactorily constant during any one day although over a long period it showed some drift, probably due to reduction of the diameter of the filament due to evaporation.

Measurements were made by the second Drude method as modified by Coolidge[23] and yielded an accuracy well within one per cent. The reproducibility of results depended largely on the character of the solution investigated, being excellent for sucrose solutions and rather disappointing for V_2O_5 sols, probably due to precipitation on the electrodes. With sucrose the deviations of single values from the average were within 0.2%. Although the method adopted is probably the best, it has the serious disadvantage for very sensitive colloidal solutions that any modification of the solution in the immediate neighborhood of the electrodes is much magnified in the results.

When the frequency of alternation of the field becomes so great that the polar molecules lag behind, dielectric absorption occurs. In the study of the thixotropic solutions, it is evident that at frequencies where absorption occurs the greater relaxation time of molecules within the sphere of influence of the particles will produce enhanced absorption, unless the frequency used is greater than the frequency of the maximum absorption. Measurement of absorption has the advantage that a small change in relaxation time can be detected at a greater wave-length than by measurement of dielectric constant if the percentage accuracy in the two cases is the same. Absorption measurements were accordingly made on all the solutions investigated. Unfortunately, the logarithmic damping decrement did not prove to be constant over the whole resonance curve with the particular set-up used and consequently the absorption measurements do not carry the weight that they should otherwise have. Also there occurs an anomalous absorption band for water at the wave-length produced by the tube, and that reduced the accuracy of the measurement of the small effect sought.

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[19] P. Drude: Z. physik. Chem., **23**, 297 (1897).

[20] Nichols and Tear: Phys. Rev., (2) **21**, 587 (1923).

[21] For a good summary of methods for generating high frequencies see W. H. Moore: J. Franklin Inst., **209**, 473 (1930).

[22] K. Kohl: Ann. Physik, (4) **85**, 1 (1928).

[23] W. D. Coolidge: Ann. Physik, (3) **69**, 125 (1899); see also G. Potopenko: Z. Physik, **20**, 21 (1923), who has discussed the method and given equations. He has paid particular attention to absorption.

Temperature as a factor was ruled out by making all of the measurements in a constant temperature room where the daily fluctuation amounts to 0.2°

Three measuring condensers of different sizes were used, each calibrated against solutions of acetone in water which Drude[24] found to have practically a linear relationship between per cent by weight and dielectric constant.

As fiducial value for the dielectric constant of water at 17.5°, the room temperature, that of Coolidge[25] was taken, viz., 81.5. The value of 21.3 for acetone was taken from the measurements of Colley.[26]

Experimental Results

Al_2O_3. Aluminum oxide sols made by Gann's method (the hydrolysis of aluminum acetate) are quite stable and are readily made thixotropic by the addition of electrolyte.[27] Upon shaking the gel it becomes a fluid of low viscosity which resets to a gel again on standing. A well dialyzed sol was divided among eight well cleaned test-tubes with ground glass stoppers and solutions of K_2SO_4 added drop by drop with shaking until the concentration of the Al_2O_3 was reduced to 0.97%, while that of K_2SO_4 varied from tube to tube from 0.16 to 1.64 millimols per liter. The solutions containing 1.34 millimols per liter K_2SO_4 or more were thixotropic.

TABLE III

Millimolar conc. K_2SO_4	Dielectric Constant	Millimolar conc. K_2SO_4	Dielectric Constant
0.00	81.1*	0.89	80.4
0.16	80.55	1.34	80.1*
0.45	80.55*	1.64	79.8*

* Ave. of several measurements.

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[24] P. Drude: Z. physik. Chem., **23**, 288 (1897).

[25] W. D. Coolidge: Ann. Physik, (3) **69**, 134 (1899).

[26] A. R. Colley: Physik. Z., **11**, 324 (1910).

[27] H. Freundlich and L. L. Bircumshaw: Kolloid-Z. **40**, 19 (1926).

Fig. 2 and Table III represent the results of the measurements of dielectric constants. It will be noted that the first small addition of electrolyte produces a much larger depression of the dielectric constant in proportion than additions thereafter.

Although numerous measurements were made with the greatest possible care on the thixotropic sols before and after gelling, they showed the same dielectric constant within the experimental error.

Absorption measurements indicated only that the absorptions in the sols and gels in water are the same within 2-3%.

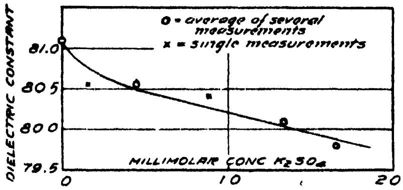

FIG. 2
Aluminum Oxide

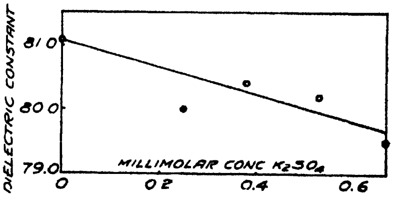

Fig. 3
Ferric Oxide

To make sure that the above effects were not due to the K_2SO_4 in solution, a 1.64 millimolar solution of K_2SO_4 in pure water was measured, and showed a dielectric constant of 80.9 and an absorption of 6% higher than water. The probabilities are that most of the K_2SO_4 in the Al_2O_3 sols is adsorbed so that the disturbance due to that in solution is negligible.

Fe_2O_3. The most completely studied of the thixotropic gels are those of Fe_2O_3[5,2]. A commercial sample made by the hydrolysis of $FeCl_3$ was dialyzed through cellophane for 20 days and then made up into portions with different K_2SO_4 concentrations and an Fe_2O_3 content of 3%. The longer dialysis of such a sol is pursued, the less electrolyte is required to give it thixotropic properties, and also the more readily it is precipitated. The ease of precipitation probably accounts for the relatively low accuracy of the results.

Table IV and Fig. 3 show the results of measurements on one series of sols. The general decrease in dielectric constant with increasing quantities of K_2SO_4 is quite plain. Sols with 0.5 millimols per liter of K_2SO_4 or more were thixotropic.

TABLE IV

Conc. K_2SO_4 millimols/l	Dielectric constant	Conc. K_2SO_4 millimols/l	Dielectric constant
0.00	81.1	0.53	80.2
0.25	80.0	0.67	79.5
0.38	80.4		

Again numerous measurements were made on the same sols both before and after gelling. The results indicate that the gels may have constants 0.2 higher than the sols, but that is a smaller difference than the probable experimental error so cannot be relied upon.

The absorption was found to be the same as in water.

Bentonite. Natural Bentonite forms a thixotropic gel when above 7-8% concentration.[8] By dialysis it loses this thixotropy which can be revived by the addition of electrolyte. In this case the most effective salts are those with polyvalent cations.

The dielectric constant of a 7.1% sol remained constant at 72.6 with increasing concentrations of $CaCl_2$ up to 1.7 millimolar.

The absorption in the dialyzed sol was 10% greater than in water and increased steadily with increasing $CaCl_2$ concentration to 20% greater than water at 1.7 millimolar.

Although the Bentonite had been dialyzed for two weeks in 0.03 mm. thick cellophane, the removal of electrolyte was not complete enough to completely destroy thixotropic properties, so no figure can be given on the minimum concentration of $CaCl_2$ necessary to bring it about.

V_2O_5. The V_2O_5 sol was made according to the Biltz method[28] (the treatment of ammonium vanadate with HCl, washing and peptizing with water). The sol was over 3 years old so that all ageing effects should have already occurred. It was dialyzed 11 days before using.

As stated earlier, it was very difficult to obtain concordant results due, no doubt, to precipitation on the electrodes. A film of V_2O_5 was readily detectable over the electrodes after a measurement. The average of numerous measurements on a 0.9% dialyzed sol gave a dielectric constant of 81.0, while the dielectric constant for a sol of equal concentration made 2.2 millimolar in KCl was 82.2.

This is the only sol showing high absorption. Both the 0.9% dialyzed sol and sol containing the KCl showed 100% greater absorption than water.

Gelatin. Since gelatin is a representative of the hydrophile colloids and represented by Keller[15] as having a very large affect upon the dielectric constant at a wave length of 76 cm., two solutions of Agfa color filter gelatin of 0.55 and 1.10% concentration respectively were measured. The results are compared with those of Keller in dilute solution in Table V.

TABLE V

Keller		Author	
Conc.	D.K.	Conc.	D.K.
1.9%	74.9	0.55	80.7
4.8	68.3	1.10	79.9

Such a large difference in values is hard to explain. It is to be noted that Keller, using the same apparatus, obtained the objectionable results for sucrose recorded earlier.

Marinesco's[29] figures at 6.5 m. on the other hand show a maximum in the dielectric constant-concentration curve at 0.6% gelatin, which he ascribes to a large dipole moment in the single gelatin molecules. That a molecule of 10,000 molecular weight[30] could display its dipole in a field of such rapid oscillations seems possible since the relaxation time varies directly as the volume of the molecule.[31] If as a rough approximation it is assumed that the ratio of the relaxation times of gelatin and water is that of the molecular weights, gelatin should display anomalous dispersion at a wave length 500 times as great as for water. The region for water practically lies between 0.1-10 cm. which would place it roughly between 50-5000 cm. for gelatin. Due to the highly hydrated character of the gelatin molecule, one would not expect its density to be large and 6.5 meters should be on the high frequency side of its anomalous dispersion range.

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[28] H. Freundlich: Colloid Symposium Monograph, 2, 46 (1925).

[29] N. Marinesco: Compt. rend., 188, 1163 (1929).

Sucrose. Although a study of sucrose does not properly belong with that of thixotropic gels, it seemed to be of sufficient interest to make measurements on its solutions since much attention has been given to its hydration.[32]

Table II and Fig. 1 give the results at two very different wave-lengths.

The absorption increases with concentration of sugar and is 6% greater than water in the 19.45% solution.

Discussion

The very definite slope to the curves for Al_2O_3 and Fe_2O_3 indicate that the previous assumption of increased hydration due to the addition of electrolyte to these sols is correct. The dielectric constants of the dialyzed sols are surprisingly near that of water. Little can be inferred from this fact except that in the absence of all but a trace of electrolyte the fraction of the water molecules seriously hindered in their adaptation to the impressed field is too small to be measured in the present experiments.

The first small addition of electrolyte affects a larger relative change in hydration than subsequent additions, which might be expected from a consideration of the probable connection with adsorption of the ions on the micelles. One would also expect the curves to flatten out with larger quantities of electrolyte. In the cases of Al_2O_3 and Fe_2O_3 this expectation would probably be realized if a suitable correction were introduced for the electrolyte effect on the dielectric constant at the higher concentrations. With Bentonite where one can reasonably assume some electrolyte already present, the curve is found flat.

Whether the increase in hydration and the decrease in stability of these sols are intimately connected or merely independent results of the same cause is uncertain but one is inclined to feel that the latter is more nearly correct. If the sol is considered to have two sources of stability affected by the addition of electrolyte, viz., the electrostatic repulsion between the charged particles and the cushioning effect of the hydration layer, the addition of electrolyte will serve on the one hand to decrease the stability due to the reduction of

[30] E. J. Cohn: J. Biol. Chem., 63, 721 (1925).

[31] P. Debye: "Polar Molecules," pp. 84-85 (1929).

[32] J. W. McBain and S. S. Kistler: J. Phys. Chem., 33, 1806-12 (1929).

charge on the particle and on the other hand to increase the stability by increasing the hydration layer. What the sum total effect will be with very small additions of electrolyte cannot at present be predicted. With large additions it is to destroy the stability. The course of the stability curve might very well go through a maximum.

If the stability of the sol is reduced by some other means than the addition of electrolyte, the decrease will probably be, in part at least, due to the reduction of charge.[33] The increase in hydration, if any, does not completely compensate for the decrease in charge. Now when electrolyte is added the sol is found very much more sensitive to it because of the already diminished charge. One must assume that hydration alone cannot maintain the dispersion of hydrophobe particles. This prediction is very well confirmed by the behavior of Fe_2O_3 sols. A sol that has been dialyzed a long time is several times as sensitive to the addition of electrolyte and the thixotropic gel formed is coagulated by much shaking, whereas a gel made from not too long dialyzed sol stands a great deal of shaking without effect. The hypothesis that the degree of hydration increases with the decreasing total stability is borne out by the fact that the longer an Fe_2O_3 sol is dialyzed before the addition of electrolyte, the smaller is the concentration of the Fe_2O_3 necessary to produce a thixotropic gel.

(Dialysis and addition of electrolyte seem to be antagonistic treatments, but it must be borne in mind that the Fe_2O_3 sols made by the hydrolysis of $FeCl_3$ are really colloidal basic chloride with a certain tendency to decompose irreversibly. Colloidal solutions of pure Fe_2O_3 of the concentrations used cannot be produced.)

One would look immediately to the absorption measurements for confirmation of the conclusion that addition of electrolyte to Al_2O_3 and Fe_2O_3 sols increases hydration. A lack of an increase in absorption would not disprove the above findings since if the water molecules affected are altogether prevented from following the field, no absorption will occur; however, one would expect many of the molecules to be only partially hindered and consequently act as absorbers. It is unfortunate that the most convenient method of producing high frequency should have produced a wave-length lying in an absorption band of water, and also that the logarithmic damping decrement could not be exactly determined with the given set-up.

Probably the most important conclusion to be drawn from the measurements is that there is no measurable change in the degree of hydration as represented by dielectric constant and absorption measurements when a sol sets to a gel. This means that the internal viscosity of the gels is very little, if any, higher than that of the sols, since the measure of what we have chosen to call the degree of hydration has been nothing more nor less than a measure of the change in the viscosity of the medium experienced by the water molecules themselves.[31]

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[33] B. N. Ghosh (J. Chem. Soc., 1929, 2693) finds that whether precipitation of an Fe_2O_3 sol is produced by the addition of univalent or divalent salts or by the addition of AmOH, at the point where rapid precipitation occurs the zeta potential has been reduced to practically the same value.

Measurements on the 1.1% gelatin sol before and after gelling lead to the same conclusion. The fluidity of the solution in the interstices of the gelatin gel is very nearly the same as that between the micelles before setting, and not widely different from that of pure water.

The behavior of V_2O_5 sols was to be expected. Errera[34] has found them extraordinarily polar at long wave-lengths, the polarity extending down to such short wave-lengths as to exclude any possibility of its arising from a fixed dipole in each colloidal particle.

Szegvari and Wigner[35] have probably rightly placed this polarity as arising from surface conductivity of the elongated particles greater than that of the surrounding medium so that ions can migrate along their lengths and produce charges on their ends. The calculations of Szegvari and Wigner have been given a more acceptable mathematical foundation by Bikerman.[36] If one uses the assumptions of Bikerman's as to possible size of the particles and introduces surface conductivity of the order of magnitude of that found by McBain and Peaker[37] for glass and fused silica in 0.001 N KCl, he can qualitatively duplicate the curve of dielectric constant against frequency found by Errera.

The increase in dielectric constant of the V_2O_5 sols with addition of electrolyte is readily explained on the ground of increased surface conductivity, while the large absorption is to be expected, both due to the surface conductivity of the particles and to the fact that the V_2O_5 is precipitated by the alternating charges and forms a film on the electrodes. Any hydration effects are completely obscured.

In order to see how great a change of relaxation time the above figures would represent, two calculations were carried out using the equations of Debye relating dielectric constant, absorption and relaxation time.[38] In the first calculation an increased absorption of 10% was assumed, and it was further assumed that all of this increase in absorption is due to change of relaxation time. In view of the fact that at the wave-length of 32 cm. there is more absorption than would be predicted from the Debye calculations, a large element of uncertainty enters since there is no way of predicting whether or not a change in relaxation time will be accompanied by a change in the other properties producing absorption. If, as above, the 10% increase in total absorption is ascribed solely to a change of relaxation time, it would represent an increase in this time of 70%.

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[34] J. Errera: Kolloid-Z., **32**, 157 (1923).

[35] A. Szegvari and E. Wigner: Kolloid-Z., **33**, 218 (1923).

[36] J. J. Bikerman: Physik. Z., **27**, 769 (1926).

[37] McBain and Peaker: J. Am. Chem. Soc., **51**, 3294 (1929).

[38] P. Debye: loc. cit., p. 92.

The second calculation showed that a five-fold increase in the relaxation time would decrease the dielectric constant measured at 32.7 cm. wave-length by approximately one unit. From the measurements on the Al_2O_3 and Fe_2O_3 sols it is safe to say that the reduction of dielectric constant ascribable to hydration is less than one unit so that the maximum effect that the sol particles can have upon the relaxation time of the bulk of the water is a five-fold increase. Probably half that value is more nearly correct. In other words, the viscosity of the water between the micelles in one of these thixotropic gels is of the order of three times that of pure water. Any change that may occur upon gelation must be a small one.

Even though it has been shown that when a hydrophobic sol is brought to the thixotropic condition an increase in hydration occurs, it can be reasonably questioned whether this hydration is sufficient to account for gelation. If, however, chains of water molecules tend to extend out from the surfaces of the micelles, it is reasonable to suppose that when sufficient of these chains exist and a solid support, such as the walls of the containing vessel, is sufficiently close, the mass of micelles would tend to be linked into a complicated network that would possess some resistance to deformation.

The network of chains of water molecules between the micelles would tend to draw them together, while electrical charge would resist this tendency and a state of equilibrium would be attained. Upon too large reduction of charge by addition of electrolyte, the repulsion could no longer balance the pull and coagulation would occur.

When one considers that the tensile strength of water is of the order of thousands of kilograms per square centimeter, it is obvious that only a very small fraction of the total water present need be connected in chains at any one instant. The observed phenomena in thixotropic gels are quite in harmony with this assumption of connecting chains.

That some sort of anisotropy exists in ordinary liquids is very strongly indicated by recent X-ray investigations. For example, Stewart[39] finds that if one assumes that the molecules group themselves into evanescent associations resembling crystallites the observed phenomena are most readily explained. Even in such a liquid as mercury where association is ordinarily assumed to be very small or absent Debye[40] finds definite maxima in the molecularly scattered X-rays and is of the opinion that "the clarity of these maxima must be connected with a certain regularity of the arrangement of the molecules themselves in the liquid, a regularity which perhaps reminds one of the grating arrangement of atoms in solid crystals".

Whether the phenomena observed are due merely to rythmical density variations in the liquid with orientation of the molecules or possibly to linkage of molecules into chains, it is perhaps too early to state, but the important fact for consideration here is that in all probability this anisotropy would tend to extend from an orientating surface, and under suitable circumstances could give rise to the phenomenon of thixotropy observed in gels.

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[39] G. W. Stewart: Phys. Rev., 32, 558 (1928).

[40] P. Debye: Paper before the Deutsche Gesellschaft für technische Roentgenkunde, Heidelberg, June 2-3, 1930.

In this place I should like to express my gratitude to Professor H. Freundlich for permission to work in his laboratories and for kind advice and interest in the progress of the work, and also to H. Kallmann for the use of apparatus and for much friendly assistance. I am also indebted to the American-German Student Exchange for funds which greatly aided in the pursuit of the problem.

Summary

Hypotheses of the origin of thixotropy in gels are reviewed, and the assumption that hydration is at least a contributory cause is favored.

Calculation of degree of hydration from dielectric constant measurements is discussed and it is emphasized that the results obtained depend directly upon the frequency of oscillations in the measuring circuit. The influence of hydration on the dielectric constant is shown to be probably due to a direct influence on the relaxation time of the water molecules near a hydrated molecule or micelle due to their orientation and their tendency to link together. Electrical saturation effects are probably minor. No quantitative values for the degree of hydration can be given without the introduction of some arbitrary definition or the arbitrary selection of conditions of measurement.

The influence of hydration on dielectric constant will be greater the greater the frequency of the measuring circuit, reaching a maximum where the slope of the dielectric constant-frequency curve is a maximum.

Measurements on dialyzed Fe_2O_3 and Al_2O_3 sols at 32.7 cm. wave-length show little, if any, hydration but give quite definite indications of hydration in the presence of small concentrations of electrolyte.

In none of the cases studied is the viscosity of the intermicellar solution measurably higher in the gel than in the sol before gelling, nor is this viscosity widely different from that of water.

Thixotropy is most readily explained by the assumption that some form of orientated anisotropy of the water, probably chains of water molecules, extends out from the surface of each colloidal particle and tends to link it with the neighboring particles.

Kaiser Wilhelm Institut für
physikalische Chemie und
Elektrochemie, Berlin.
June 30, 1930.

NEPHELOMETRIC TITRATIONS. II

The Standard-Solution End-Point*

A previous paper[1] from this laboratory has called attention to a possible source of error in the equal-opalescence end-point used in nephelometric atomic weight titrations. It is the purpose in the present article to suggest an alternative end-point for such titrations, free from this source of error, and possessing certain other advantageous features. To distinguish the proposed end-point from the other, it may be termed the standard solution end-point.

The proposed standard solution method differs from the equal-opalescence method only in the determination of the end-point of the reaction under investigation. That is, one precipitates an acid solution containing the chloride (or bromide) ions from a weighed quantity of a pure compound in the usual manner, using within a few tenths of a milligram of the theoretical amount of pure silver, weighed, and dissolved in nitric acid. At this stage, without necessarily making further additions to the system, one determines the end-point by measuring the *absolute* amounts of silver and halide ions in the supernatant liquid. This is done by comparing test portions of the supernatant liquid with standard solutions having practically the same composition as the supernatant liquid itself, with the aid of the nephelometer.

In each individual titration, two sets of standard solutions are required, for the determination of the silver and the halide, respectively, in the test portions of the analytical solution. The details of the preparation of these standards must, of course, vary with the particular "atomic weight" ratio under investigation. The general procedure in the use of the proposed end-point may be inferred from the tests described below. It may be noted that all of the water and nitric acid used in these experiments was purified by the methods usually employed in atomic weight determinations.

Experimental

A number of 18 gm. portions of pure silver nitrate were dissolved in 1100 cc. volumes of water in glass-stoppered 3-liter Pyrex Erlenmeyer flasks and precipitated at the rate of about 4 cc. a minute with equal volumes of hydrochloric acid containing a slight excess of HCl. The precipitates, after standing, were washed about 20 times with 300 to 500 cc. portions of water, with intermittent soaking and shaking during a period of a week. After this time, varying calculated amounts of nitric acid were added to the flasks, and the volume was in each case made up to 1500 cc. with water. The solutions were then saturated with silver chloride by intermittent shaking over a period of several days.

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* Contribution from the Chemistry Department of The Rice Institute.

** National Research Fellow in Chemistry.

[1] Johnson: J. Phys. Chem., 35, 540 (1931).

The silver and chloride content of each solution at approximately 0°C. was determined as follows. The flask containing the solution was partially immersed in an ice-salt bath until the contents had completely frozen. It was then removed, carefully washed, and allowed to stand in air until about three-fourths of the contents had melted, whereupon it was placed in a bath of cracked ice and allowed to stand, usually for at least eight hours, with occasional gentle but thorough shaking. About two hours after the final shaking, 400 cc. of the clear supernatant liquid were withdrawn with a pipette and placed in a Pyrex bottle, which had been cleaned, dried, and rinsed with a small amount of the liquid. In other cases the solution was not frozen, but was withdrawn after cooling in an ice bath for several hours, with frequent shaking. Some preliminary experiments showed the inadvisability of removing the flask from the ice bath until after the sample had been withdrawn, even for the purpose of shaking the solution. The sample was allowed to stand overnight before making the nephelometric tests, as it was also found important that it should be at exactly the same temperature as the standard solutions used in its analysis.

The acid concentration of each sample was next determined by titration of 25 cc. to 100 cc. portions with 0.505 M sodium hydroxide, using methyl orange as an indicator. The chloride and silver content of each of the samples was determined by nephelometric tests, which consisted in comparing 22.00 cc. portions of the samples with standard solutions of equal volume. These standards were prepared from pure water, 5.16 M nitric acid, and solutions made by diluting measured volumes of primary standard solutions of silver nitrate or sodium chloride containing 1.000 mg. of silver or its equivalent per cc. In all of the volumetric measurements calibrated apparatus was used, of dimensions intended to give the measurements, without exception, a precision of 1 part in 500 or better.

In analyzing for chloride, the standard and test solution were precipitated with two equal 1.00 cc. portions of the primary standard solution of silver nitrate; in analyzing for silver, the standard and test solution were precipitated with two equal 1.00 cc. portions of the primary sodium chloride standard. In the precipitation of the solutions, and in reading the nephelometer, the precautions given by Richards and Wells[1], and Wells,[2] were observed. The procedure employed was adapted from that described by Scott and Johnson,[3] with slight modifications to make it suitable for the present experiments. The silver chloride used in this work, except the minute amounts employed in nephelometric tests, was illuminated only by red light.

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[1] Richards and Wells: Am. Chem. J., **31**, 235 (1904); J Am. Chem. Soc., **27**, 484 (1905).

[2] Wells: Am. Chem. J., **35**, 99 (1906).

[3] Scott and Johnson: J. Am. Chem. Soc., **52**, 2644 (1930).

The typical data of a single analysis is given below in condensed form:

Analysis of Sample from Flask No. 1

Sample: 400 cc. of solution; frozen; melted; cooled for 9 hours; withdrawn at 1.0° C.; warmed to 30° C. Found to be 0.485 M in nitric acid at 30° C.

Test Solution: 22.00 cc. of above sample.

Standard Solution: Made from 2.07 cc. of 5.16 M nitric acid and 19.93 cc. of sodium chloride solution containing the equivalent of 0.001124 gm. of AgCl per liter. It thus contained sodium chloride equivalent to 0.00102 gm. of AgCl per liter, in 0.485 M nitric acid, at 30° C.

One hour after precipitation of the two solutions with excess silver nitrate, the mean of 20 settings gave a value of 1.01 for the nephelometric ratio, with an average deviation of 0.025 unit. The standard tube had the weaker opalescence.

Therefore the test solution contained 0.00103 gm. of AgCl per liter.

The results of other similar analyses are given in Table I. Each result recorded in the table corresponds to a set of 20 nephelometric readings, made with an independently-prepared standard and a fresh portion of the sample.

Analysis of Silver Chloride Solutions

Table I

Molarity of sample in HNO_3	Time of cooling Hours	Temp. at removal Corr °C.	Ratio	Nephelometer Ratios and Grams of AgCl per liter: Found as NaCl	Ratio	Found as $AgNO_3$
			Part 1			
0.000	10	0.5	1.40	0.00106	1.00	0.00104
	10	0.4	1.34	0.00101	1.07	0.00111
0.111	6	0.4	1.68	0.00172	1.68	0.00173
	14	0.4	1.10	0.00093	1.35	(0.00138)
0.241	3	1.4	1.55	0.00197	1.31	0.00238
	3	1.4	1.14	0.00217		
0.485	6	0.5	1.54	0.00186	1.16	0.00148
	6	0.5	1.08	0.00166		

TABLE I (Continued)

Molarity of sample in HNO_3	Time of cooling Hours	Temp. at removal Corr °C.	Ratio	Nephelometer Ratios and Grams of AgCl per liter:		
				Found as NaCl	Ratio	Found as $AgNO_3$
			Part 2			
0.000	9	0.4	1.35	0.00077	1.63	0.00064
	9	0.4	1.33	0.00078	1.53	0.00068
			Average	0.00078		0.00066
0.111	8	0.6	1.00	0.00091	1.18	(0.00077)
	8	0.6	1.01	0.00092	1.01	0.00092
	8	0.6	1.04	0.00094	1.06	0.00086
			Average	0.00092		0.00089
0.241	6	0.6	1.13	0.00100	1.16	0.00103
	8	0.6	1.10	0.00098	1.15	0.00102
			Average	0.00099		0.00103
0.485	1	0.5			1.45	(0.00100)
	6	1.0	1.08	0.00109	1.14	(0.00089)
	9	1.0	1.01	0.00103	1.02	0.00104
	9	1.0			1.02	0.00100
			Average	0.00106		0.00102
0.988	8	0.4	1.08	0.00100	1.01	0.00107
	8	0.4	1.03	0.00104	1.04	0.00104
	8	0.4	1.04	0.00103	1.02	0.00110
			Average	0.00102		0.00107

Part 1 of the table includes analyses of solutions cooled without freezing; Part 2 includes analyses of solutions frozen and melted before cooling. The nephelometric measurements were made at temperatures varying from 30° to 33° C. For purposes of comparison, both of the constituents determined have been calculated as AgCl. The nephelometric ratios included in the table show only the relative compositions of the standard and test solutions, as the ratios have been calculated so that they are uniformly greater than unity. No analyses have been omitted; the bracketed values I am inclined to reject.

While the tests described above were not intended primarily as solubility measurements, it is interesting to note that the data in Part 2 of Table I form a consistent set of determinations of the solubility of silver chloride in varying concentrations of nitric acid. Giving each independent analysis equal weight, and reducing all of the values to 0.5° C., the data combine as follows:

Temp.	Molarity of Nitric Acid	Gm. AgCl per liter
0.5	0.000	0.00072
0.5	0.111	0.00090
0.5	0.241	0.00100
0.5	0.485	0.00102
0.5	0.988	0.00105

Discussion of Results

It seems reasonable to conclude that the data in Table I show that the standard solution end-point is suitable for use in nephelometric atomic weight titrations. In solutions at the stoichiometrical point (saturated silver chloride solutions) the method indicates that the silver and chloride ions are equal, with the desired precision. That is, the average silver and chloride, calculated as AgCl, agree within a few hundredths of a milligram, when the tests are made under the proper conditions (Table I, Part 2).

These conditions, as defined by the present experiments, may be summarized: (1) The cooling of the solutions should be preceded by freezing and melting. This treatment hastens the attainment of equilibrium, decreases the amount of dissolved material to be determined, and reduces the measurements to a common basis. The latter feature may prove of value in detecting any abnormality in the end-point of the titration. (2) In general, the measurements become somewhat more dependable as the nephelometric ratio approaches 1.00. It follows that successively-prepared standards should approximate more and more closely to the test solution in composition. In any case, in the determination of each constituent the analyses should be made at least in triplicate, with fresh, independently-prepared standards. (3) In every analysis the standard and test solutions should be at exactly the same temperature. (4) Acid concentrations between 0.3 M and 1.0 M are suitable for use in the analytical solutions. (5) The method used in preparing the standard solutions evidently involves no serious error. Nevertheless, the possibility of introducing improvements and refinements in the method is apparent. The use of solutions of silver chloride as primary standards has been considered.

It is recognized that in some atomic weight determinations the preparation of standard solutions containing suitable amounts of the "extra" ions present in the analytical solutions may involve difficulties. However, in all but exceptional cases it should easily be possible to prepare standards of the necessary purity with an accuracy at least ten times greater than that required. In spite of the great sensitivity of the nephelometer, nephelometric observations are accurate only to about 1 part in 50.

General Discussion

It is not the intention in this paper to imply that the possibility of an error in the equal-opalescence procedure, in certain types of titrations, affects in any way its past or present general usefulness, or that the proposed standard solution procedure is anything more than a possible alternative or supplementary one. Both methods have their characteristic advantages. For the present, attention is confined to two advantages peculiar to the standard solution method: (1) It offers the opportunity of comparing, in the nephelometric tests, systems which are practically identical in composition. The importance of this feature has often been stressed by Richards.[1] The same opportunity does not appear in the equal-opalescence method, in which one compares systems precipitated with *equivalent* rather than with *equal* amounts of the precipitating reagents. (2) In the standard solution method one measures the *absolute* amounts of silver and halide ions in the analytical solutions; in the equal-opalescence method only the *relative* amounts are found. The use of the standard solution procedure gives valuable data regarding the solubility of silver chloride in the analytical solutions, and information concerning the equilibrium between silver and halide ions in the neighborhood of the end-point. This feature is of value if the nephelometric analyses are to be followed by incidental gravimetric analyses, as it permits an exact correction for chloride lost in the nephelometric tests. Reports of such atomic weight determinations, in which it has been customary to employ the equal-opalescence method, give one the impression that this rather important correction has frequently been neglected, although corrections involving smaller quantities of material have been taken into consideration.

In conclusion, it may be said that while the measurements recorded in this paper show the essential validity of the proposed end-point, the usefulness of such an end-point can only be established by actual trial under the conditions arising in atomic weight work. Such a trial is desirable, if only for the reason that it is good policy in atomic weight investigations to gather evidence from many sources.

Summary

An end-point for use in nephelometric atomic weight titrations has been proposed. Experiments show that under a specified set of conditions the end-point corresponds to the stoichiometrical point with the desired accuracy.

Houston, Texas.

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[1] Richards: Am. Chem. J., **35**, 511 (1906). See also, Richards and Wells: Am. Chem. J., **31**, 242 (1904).

SOME PHYSICAL PROPERTIES OF THE TERNARY SYSTEM PHENOL-BENZENE-WATER*

SAMUEL H. WEIDMAN AND LLOYD E. SWEARINGEN

In this laboratory, a study is being made of the physical properties of certain liquid mixtures. Some of the physical properties of the binary systems, phenol and water[1] and phenol and benzene[2] have previously been reported by one of the authors. During the progress of other work in this laboratory, a need occurred for some surface tension data on the ternary system phenol, benzene and water. These measurements were made and it was thought desirable to determine a few other physical properties of this system while the materials were at hand.

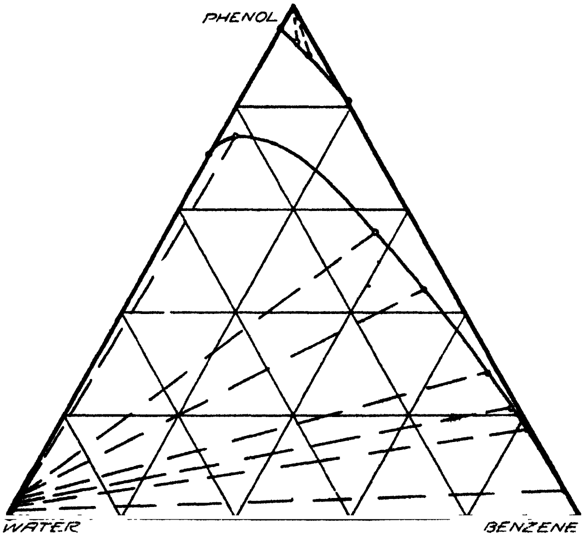

FIG. 1

Phenol-Benzene-Water.
Composition Diagram 25°C in Weight Percent (S. Horiba)

This ternary system is one for which the phase equilibrium has already been determined.[3] The composition diagram is herewith produced as Fig. 1. Measurements of the surface tension, density, viscosity and index of refraction of various mixtures, whose compositions fall within the completely miscible part of the system, have been investigated.

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* Contribution from the Chemical Laboratory, University of Oklahoma.

[1] Swearingen: J. Phys. Chem., 32, 785 (1928).

[2] Swearingen: J. Phys. Chem., 32, 1346 (1928).

[3] S. Horbia: Mem. Coll. Sci. Kyoto, 1, 49 (1914).

Experimental

Materials. The *benzene* used in these experiments was furnished by the J. T. Baker Co., and was designated as C.P. and thiophene-free. This benzene was further purified by fractional crystallization.

Phenol. The phenol used was Mallinckrodt's C.P. quality and was further purified by fractional crystallizatiom.

Water. A good grade of conductivity water was prepared and used in the preparation of the various samples.

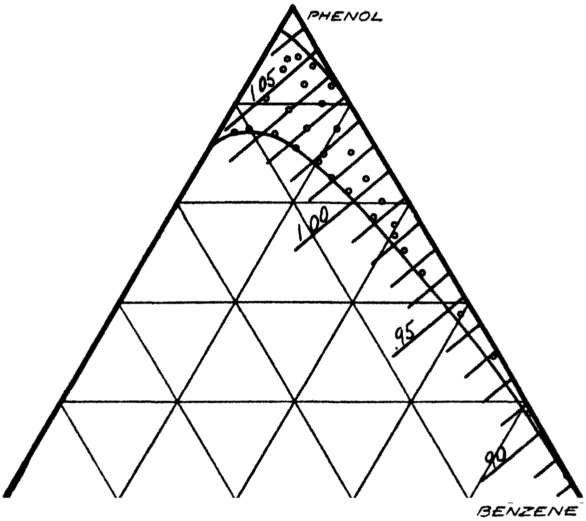

FIG. 2
Phenol-Benzene-Water.
Densities at 25°C

Preparation of Solutions

Representative points throughout the completely miscible portion of the system were selected and solutions corresponding to these compositions were prepared. All compositions are expressed on a weight basis. Thirty-one different samples were prepared. Samples numbered 9 and 13 were lost in preparation and were replaced by samples numbered 32 and 33. The compositions of the various samples are shown in Table I.

The densities were obtained by calculation from the specific gravities, measured at 25°C. with a Mohr-Westphal balance. The balance was adjusted so that water had a specific gravity of unity at 25°C. The densities calculated are those at 25°C. referred to water at 4°C. The temperature was controlled by a water thermostat, equipped with a thermo-regulator and stirrer. The temperature could be kept at 25° ± 0.1°C. with no difficulty. The specific gravity and density data are given in Table II and Fig. 2.

The viscosity measurements were made at 25°C ± 0.1°C. with a modified Ostwald-Poiseuille viscosimeter. The time of flow was determined with a stop watch which recorded time to two-fifths seconds. The data in all cases

TABLE I

Composition in Weight Percent of the Phenol-Benzene-Water Solutions

Sample No.	Percent Phenol	Percent Benzene	Percent Water
1	74.50	3.00	22.50
2	75.00	5.00	20.00
3	81.00	5.00	14.00
4	87.00	5.00	8.00
5	89.05	4.78	6.17
6	74.00	10.00	16.00
7	79.00	10.00	11.00
8	84.00	10.00	6.00
9*			
10	71.00	15.00	14.00
11	75.00	15.00	10.00
12	80.00	15.00	5.00
13*			
14	68.10	20.05	11.85
15	69.94	20.07	9.99
16	75.00	20.00	5.00
17	64.66	24.36	10.98
18	70.02	25.02	4.96
19	62.11	28.85	9.04
20	64.87	30.16	4.97
21	57.03	35.20	7.77
22	59.99	35.09	4.92
23	53.64	40.38	5.98
24	55.40	39.68	4.92
25	50.36	43.84	5.80
26	46.08	49.26	4.66
27	37.76	59.79	2.45
28	29.24	69.78	0.98
29	17.60	81.68	0.72
30	4.74	95.03	0.23
31	89.72	6.27	4.01
32	87.67	9.84	2.49
33	83.94	15.06	1.00

were reproducible to within 0.4%. Absolute viscosities were calculated from the viscosities relative to water and the absolute viscosity of water. The value 8.949×10^{-3} (in C.G.S. units) given by the International Critical Tables for water at 25°C. was used in calculating the absolute viscosities of the different samples. The viscosity data are given in Table II and Fig. 3.

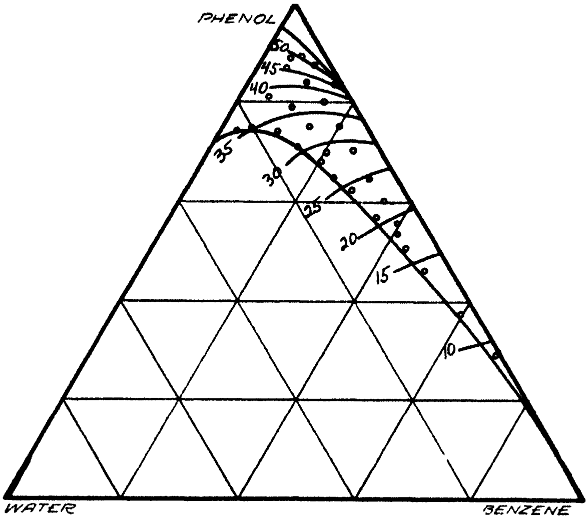

FIG. 3
Phenol-Benzene-Water. Viscosities × 10^{-3} at 25°C.

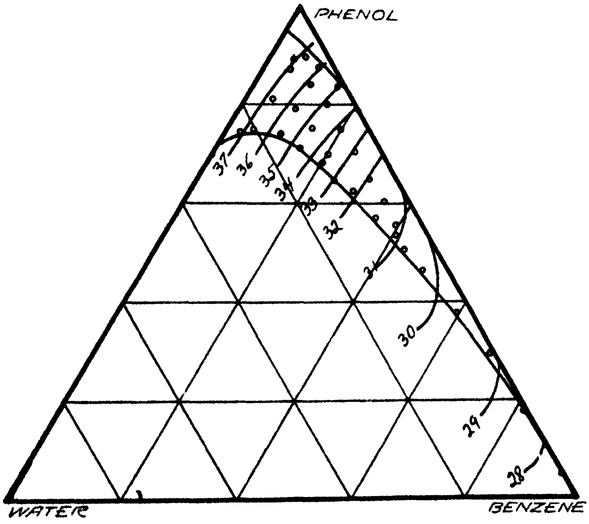

FIG. 4
Phenol-Benzene-Water. Surface Tension at 25°C.

TABLE II

The Specific Gravity, Density and Viscosity of Phenol, Benzene and Water Solutions at 25°C

Sample No.	Specific Gravity D^{25}_{25}	Density D^{25}_{4}	Relative Viscosity	Absolute Viscosity $\times 10^{-3}$
1	1.0481	1.0450	3.955	35.39
2	1.0452	1.0422	3.919	35.07
3	1.0497	1.0467	4.315	38.61
4	1.0542	1.0511	5.040	45.10
5	1.0574	1.0543	5.583	49.96
6	1.0381	1.0351	3.742	33.49
7	1 0418	1.0388	4.071	36.44
8	1.0459	1.0429	4.616	41.31
10	1.0290	1.0260	3.453	30.90
11	1.0312	1.0282	3.653	32.69
12	1.0354	1.0324	4.184	37.44
14	1.0212	1.0183	3.228	28.88
15	1.0224	1 0195	3.233	28.99
16	1.0248	1.0218	3.597	32.19
17	1.0116	1 0087	2.927	26.20
18	1.0161	1.0131	3.210	28.73
19	1.0047	1.0017	2.637	23.60
20	1.0048	1.0019	2.768	24.77
21	0.9923	0.9894	2.349	21.02
22	0.9945	0.9916	2.435	21.80
23	0.9830	0.9802	2.122	18.99
24	0 9855	0.9827	2.170	19.42
25	0.9765	0.9737	1.943	17.32
26	0.9657	0.9629	1.711	15.31
27	0.9463	0.9436	1.338	11.98
28	0.9287	0.9260	1.096	9.80
29	0.9075	0.9049	0.876	7.40
30	0.8841	0.8815	0.706	6.31
31	1.0562	1.0531	5.852	52.37
32	1.0470	1.0501	5.645	50.52
33	1.0400	1.0370	5.030	45.01
Water	1.0000	0.99707*	1.000	8.949*
Benzene		0.8734*	0.6668	5.967
Phenol		1.071*	9.952†	89.06

* Data from International Critical Tables.

† Experimental value obtained on supercooled phenol.

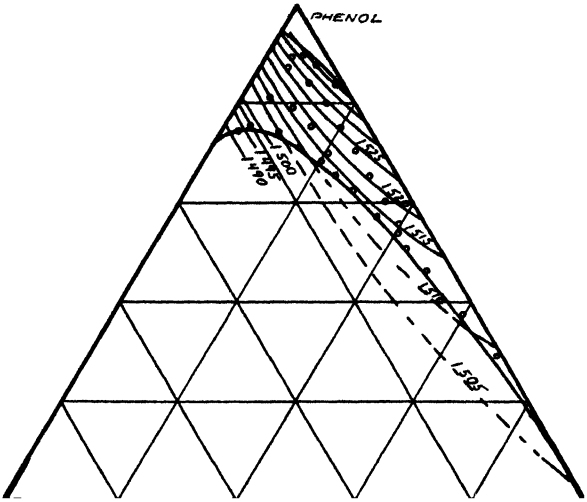

FIG. 5
Phenol-Benzene-Water. Indices of Refraction at 25°C.

TABLE III
The Surface Tension and Index of Refraction of Phenol, Benzene and Water Solutions at 25°C

Sample No.	Surface Tension dynes/cm.	Index of Refraction	Sample No.	Surface Tension dynes/cm.	Index of Refraction
1	37.15	1.4934	19	32.29	1.5132
2	36.59	1.4975	20	31.77	1.5219
3	36.87	1.5114	21	31.25	1.5121
4	36.98	1.5251	22	31.68	1.5193
5	37.26	1.5301	23	31.17	1.5116
6	35.48	1.5046	24	31.29	1.5159
7	35.87	1.5162	25	30.84	1.5134
8	35.75	1.5271	26	30.34	1.5121
10	34.36	1.5075	27	29.55	1.5116
11	34.63	1.5185	28	29.27	1.5097
12	34.92	1.5296	29	28.32	1.5047
14	33.52	1.5114	30	27.60	1.5001
15	32.72	1.5156	31	37.04	1.5372
16	33.88	1.5269	32	36.48	1.5402
17	32.96	1.5120	33	35.36	1.5412
18	33.41	1.5243	Water	71.97*	1.3325*
			Benzene	27.263**	1.4997
			Phenol	38.38†	1.5425††

* Data from the International Critical Tables.

** Fischler: Z. Elektrochemie, 19, 128 (1913).

† Experimental data on supercooled phenol.

†† at 41°C.

The surface tension measurements were made at 25° C ± 0.5°C. with a du Nouy tensimeter. Since most of the surface tension values to be measured were nearer the surface tension of benzene than water, the instrument was calibrated with benzene. With care and proper technique, the results were easily reproducible. The surface tension data are given in Table III and Fig. 4.

The indices of refraction were measured at 25°C. ± 0.2°C. with an Abbe Refractometer. These data are given in Table III and Fig. 5.

Discussion of Results

In the graphical representation of data, curves have been drawn through points having the same value of the property under consideration. Points on the phenol-benzene axis were obtained by interpolation of Swearingen's data for this binary system.

The density-concentration relation is a linear one for both of the binary systems phenol-benzene and phenol-water. This same relation also is found to hold in the ternary system. The densities of the ternary systems studied were found to be additive functions of the concentration.

The viscosities of the binary systems involved are not additive functions of the concentration and as might be expected, the data for the ternary system shows this to be the case also. The ternary system shows viscosity characteristics which partake of the characteristics of the three classes of systems into which Dunstan and Thole[1] classifies solutions. The characteristic which predominates depends upon the relative mol fractions of the components present. In the binary system phenol-benzene, the phenol exists to a large extent as associated molecules[2] thus forming a solution of the third class, in which the viscosity is less than that required for an additive effect. As water is added, there is not only a tendency to form unassociated phenol molecules, but also a tendency to form a hydrate.[3] This favors the formation of a solution partaking to some extent of the characteristics of Dunstan's second class, where the observed viscosity is greater than that required for

TABLE IV

Calculated and Measured Viscosities of Phenol, Benzene and Water at 25°C

Sample No.	Mol Fraction Phenol	Mol Fraction Benzene	Mol Fraction Water	Calculated Viscosity $\times 10^{-3}$	Measured Viscosity $\times 10^{-3}$
25	.3773	.3958	.2269	18.16	17.39
16	.5988	.1924	.2088	32.80	32.19
6	.5162	.1244	.3594	27.90	32.69
3	.5058	.0376	.4566	28.20	38.61
2	.4044	.0325	.5631	22.38	35.07

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[1] "The Viscosity of Liquids" (1914).

[2] Kwantaro Endo: Bull. Chem. Soc. Japan, **1**, 25 (1926).

[3] Smits and Maarse: Proc. Roy. Soc. Amsterdam, **14**, 192 (1922).

additive effects. In solutions rich in benzene and poor in water, the observed viscosity of the ternary system should be less and for those solutions rich in water and poor in benzene the observed viscosity should be greater than the values required for additive effects. At some intermediate composition, the two effects should be compensating and the viscosity for the ternary mixtures should become an additive function of the composition over a short range. That such a prediction is justified is shown by Table IV, where the measured viscosity is compared with the viscosity calculated on the basis of an additive effect.

Summary

The densities, viscosities, surface tensions and indices of refraction for the ternary system phenol, benzene and water have been measured at 25°C., over a wide range of concentrations within the completely miscible portion of the system.

CARBORUNDUM FRACTIONATING COLUMNS

BY ESTHER C. FARNHAM

In the spring of 1929 Thomas Midgley, Jr.,[1] published a very interesting paper entitled "Coated Spiral Fractionating Columns". "Some time ago it was observed that a Hempel column filled with a material which would behave as a 'boiling stone' in the liquid being distilled gave better results than did the customary glass beads. It was believed that varying degrees of efficiency might exist among different materials which behave as 'boiling stones'. To determine this, the following experiment was conducted: A 2-liter round-bottom flask was mounted beneath a reflux condenser and half filled with a mixture of equal parts of benzene and toluene. A thermometer, reading in tenths of a degree, was placed in the liquid and constant heat applied to the flask. After refluxing started, the temperature was observed until it became constant. This procedure was repeated with various materials as 'boiling stones' with the following results:—

Material	Temp.	Material	Temp.
No boiling stones	94.0°C	Glass beads	94.0°C
Crushed antimony	93.8	Steel strips	94.0
Crushed porcelain	92.6	Etched brass	94.0
Carborundum cloth	88.7	Etched steel	94.0
Brass strips	94.0		

"A Hempel column was then filled with small scrolls of carborundum cloth and the fractionation of benzene and toluene attempted. The results were quite unsatisfactory. It is believed that this was due to the absorption and holding of a large quantity of liquid by the cloth".

A special metal column was made containing a spiral metal strip coated with carborundum. "To measure the efficiency of this column 150 cc of pure benzene and 150 cc of pure toluene were mixed and distilled. The over-all rate of delivery was 1 cc per minute. Ninety-four percent of the benzene and eighty-six percent of the toluene were recovered, of practically the same purities as were the original materials".

The following investigation was undertaken to develop a theory concerning the high efficiency of this carborundum-coated fractionating column. The presence of a coating of carborundum seems in some way to catalyze the equilibrium between liquid and vapor so that such a column gives a very much better separation of the two liquids which are being fractioned than do ordinary columns filled with glass beads.

There are several possible explanations of this action of carborundum:—

1. There may be some correlation between the efficiency of a substance as a "boiling stone" and its efficiency as a column filling. With the "boiling

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[1] Ind. Eng. Chem., Anal. Ed., 1, 86 (1929).

stone" the important thing is the ease of formation of the vapor. Since condensation and not boiling takes place in the column, this did not seem very probable. On the other hand, it was the superior behavior of carborundum as a "boiling stone" which led Midgley to try it in the column.

2. There may be an increased rate of condensation or evaporation or both, due to the presence of sharp points. This seems plausible because reactions between vapor and solid have been shown to take place most rapidly at sharp points. Reboul[1] states that "there exists at the surfaces of separation between a system, solid and gas, adhesion forces analogous to those of capillary attraction. These forces produce at points of small radius of curvature a concentration of the gas which favors attack on the solid".

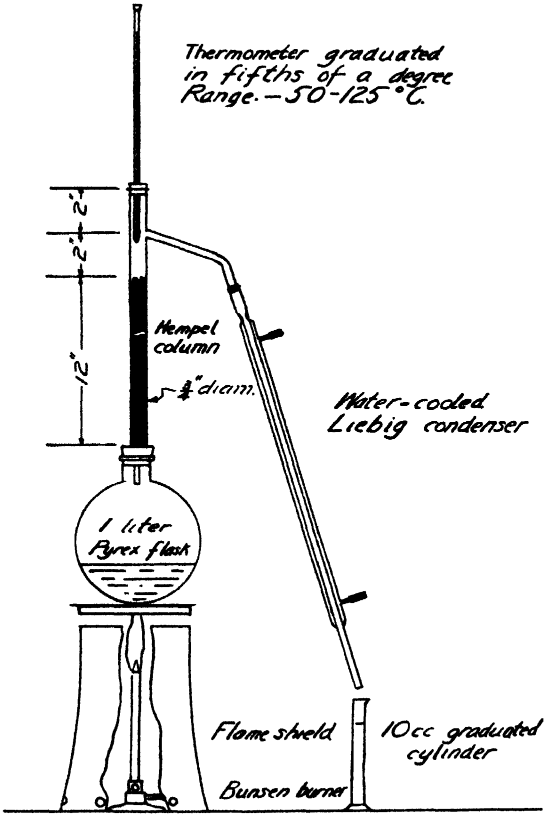

FIG. 1

It will be shown later that this factor is not the essential one in the action of carborundum, though it has some minor effect.

3. There may be a selective adsorption of vapor in the column, due to the specific adsorbing power of the material, to its crystalline structure, or to the arrangement of its surfaces.

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[1] Compt. rend., 158, 1228.

Tests were made of the efficiencies of various substances first as boiling stone and later as column filling. The results of the first of these tests were as follows:—

Material	B. Pt.	Material	B. Pt.
Glass beads	90.8°	Micaceous haematite	90.7°
Tourmaline	90.8	Carborundum chips	90.9

There was almost no effect on the boiling point of the solution even when micaceous haematite was used, though this substance was later shown to be one of the best column fillings. This is not surprising, because, as has been mentioned, we are dealing with the system vapor in liquid in the case of boiling stones, while we have the system liquid in vapor in the distilling column and are primarily concerned with increasing condensation.

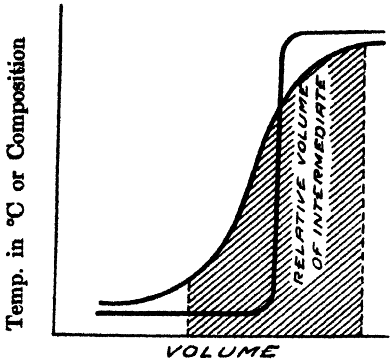

Fig. 2

In making test distillations no attempt was made to construct a very excellent fractionating apparatus. The simple set-up, Fig. 1, was used in all runs. The only precautions taken were to use the same height of column filling and to maintain a constant rate of distillation. Benzene and toluene, benzene and pyridine, pyridine and water, and, in a few cases, 95% alcohol and water were the liquid pairs used. Benzene and pyridine seemed most satisfactory because of the ease with which the distillates could be analyzed. Five cubic centimeters of the mixture were shaken in a graduated test-tube with ten cubic centimeters of dilute hydrochloric acid. The pyridine was completely soluble in the acid, and practically pure benzene separated as a second liquid layer. A number of trials with known mixtures showed this method to be accurate to within 2-4%.

In each run the distillate was collected in ten-cubic centimeter cuts; the temperature of the condensing vapor was recorded at the end of each cut; and the composition of the distillate was determined by the method described above. The curves plotted from the data thus obtained show temperature versus volume of distillate, which can be translated, if desired, into composition versus volume of distillate. In all cases where two or more curves were compared, the rates of distillation were kept as nearly alike as possible. In most cases a rate of 1.6-1.7 cc per minute was used.

In the discussions, the term "efficiency of a column" is often used. The writer understands fully that it is not used in the orthodox sense. The industrial chemist uses this term to mean the reciprocal of the height equivalent to a theoretically perfect plate.[1] I have used it in reference to distillation curves as illustrated in Fig. 2. Curve A represents almost complete separation of the two components being distilled. It may be considered an ideal case, since the volume of intermediate is practically zero. Curve B shows a poor separation with a relatively much larger volume of intermediate. A column may be called more efficient as the curve obtained approaches the form of curve A.

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[1] Peters: J. Ind. Eng. Chem., **14**, 476 (1922).

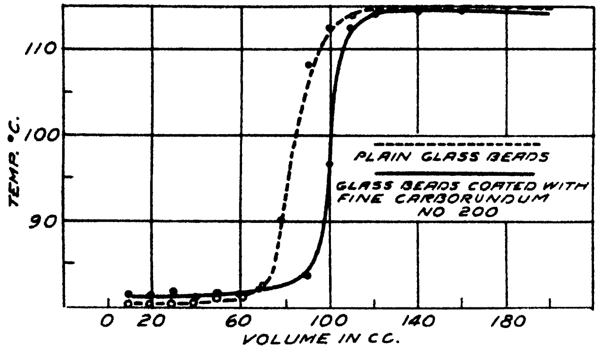

Fig. 3
Benzene and Pyridine

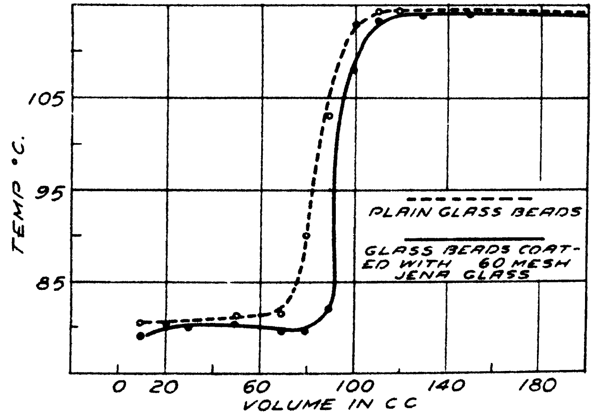

Fig. 4
Benzene and Pyridine

Carborundum occurs in flat plates with sharp edges. Micaceous haematite was picked out as coming somewhere near carborundum in structure. Needle ore is a haematite which crystallizes in needles and therefore has sharp points. A comparison of these two should show whether it was essentially a question of the chemical nature or of the shape of the crystals. A fine carborundum powder has, presumably the same composition as the coarse forms and has more edges but is less plate-like. Mica splits into thin plates and thin sheets of glass can be studied either plain or after being silvered. Alundum and tourmaline differ essentially in crystal form from carborundum and micaceous haematite. Ferrous sulphide was an after-thought.

The first set of distillation curves for benzene and pyridine, Figs. 3-6, is a study of the efficiencies of columns filled with ordinary glass beads coated with different substances. These coatings were applied by shaking the beads with 40% sodium silicate solution, draining them partially, and then shaking them with the dry material to be applied. They were then dried in an oven at 110° for several hours. After a little practice one obtains a very satisfactory coating which does not chip off easily. Shellac was also tried as a binder; but sodium silicate seems much superior. Both shellac and sodium silicate were used by Midgley. In the first run plain glass beads were used and the curve obtained was used as a standard of reference for the others.

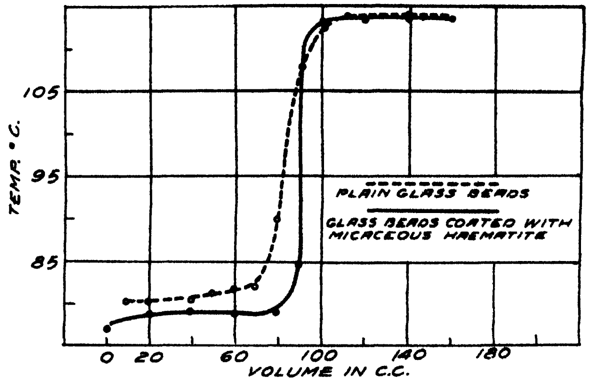

Fig. 5
Benzene and Pyridine

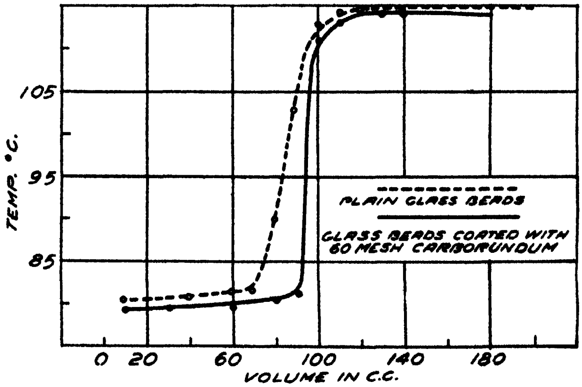

Fig. 6
Benzene and Pyridine

From the curves Figs. 3-6, it appears that:—

1. In general, a coating of rough particles on the beads gives a better fractionation than smooth beads give. This is to be expected, because there is a large increase in surface and increased friction, which tends to prolong the contact between liquid and vapor in the column, giving a better opportun-

ity for equilibrium to be reached. In connection with this it was noted that it is much easier to distill slowly at a uniform rate in a column filled with coated beads.

2. The substances vary greatly among themselves. Alundum (not shown) is not good and neither is the fine carborundum, No. 200 of the Carborundum Co. The 60-mesh Jena glass is better than the fine carborundum. On the other hand the 60-mesh carborundum is better than any of these, which confirms what Midgley found. For this particular pair of liquids, the micaceous haematite, Fig. 5, is better than the 60-mesh carborundum.

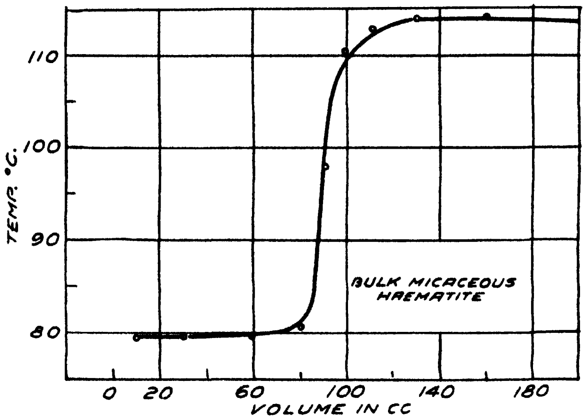

FIG. 7
Benzene and Pyridine

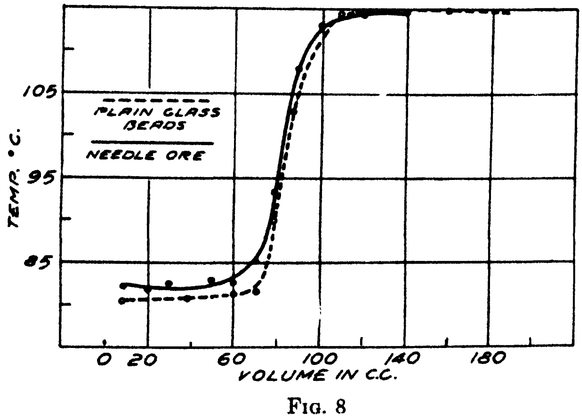

FIG. 8
Benzene and Pyridine

Since there were these marked differences between different materials, it seemed wise to eliminate the coated beads and to make another set of runs, using various substances in a crushed condition as a column filling. The materials were crushed to a convenient size with a hammer. The curves obtained from this set of runs are shown in Figs. 7-10.

Under these new conditions the carborundum and the micaceous haematite are practically equally efficient. The two curves are very close to duplicates. Both substances have the same general form, thin rhombic plates having very definite edges. Both belong to the same crystal system. Neither carborundum nor micaceous haematite (in the forms used) has especially sharp points.

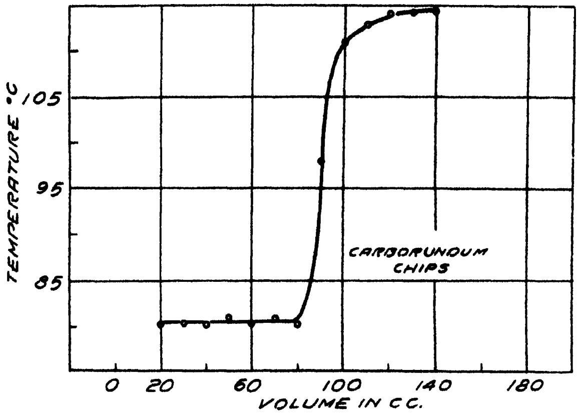

Fig. 9
Benzene and Pyridine

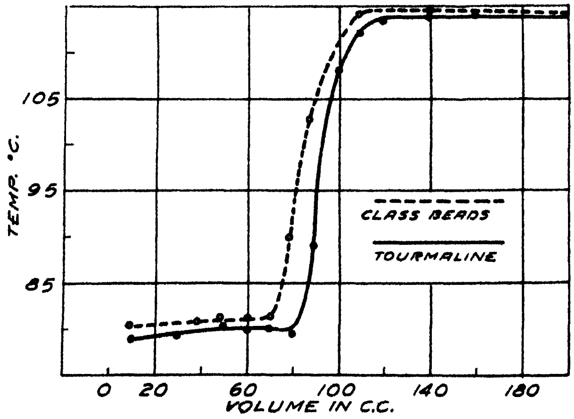

Fig. 10
Benzene and Pyridine

Needle ore, on the other hand, has extremely sharp points. It is evident, however, from Fig. 8 that needle ore is not quite so good as plain glass beads.

The evidence so far is that the form of the crystals is more important than the chemical nature. To test the possibility that thin plates make a better filling, a third set of runs was made using the following films:—

(a) Sheets of mica.

(b) Very thin glass plates made by blowing out glass bulbs almost to the breaking point and smashing the bulbs into suitably sized fragments.

(c) Glass films plated with silver.
The results of these runs are given in Figs. 11-13, using benzene and pyridine and alcohol and water.

Mica was not a success with benzene and pyridine; silver-plated glass films were better than the plain glass ones. On the other hand plain glass films were better than micaceous haematite with alcohol and water. There is, therefore, some specificity of action between the column filling and the substances being distilled. Peters[1] has shown that a given column gives different efficiencies with different pairs of liquids; but that might be a question of the form of the vapor and liquidus curves. It does not follow at all from his work that the efficiencies would vary with the packing material apart from the arrangement.

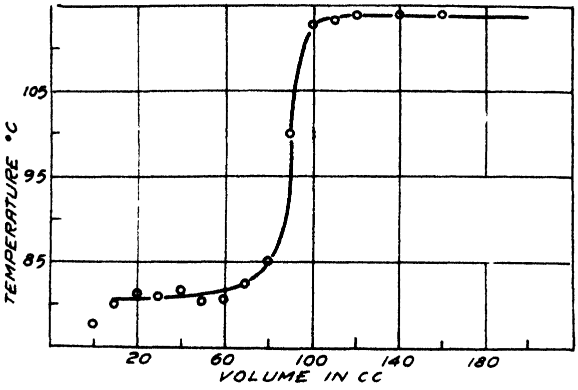

FIG. 11
Benzene and Pyridine (*Mica*)

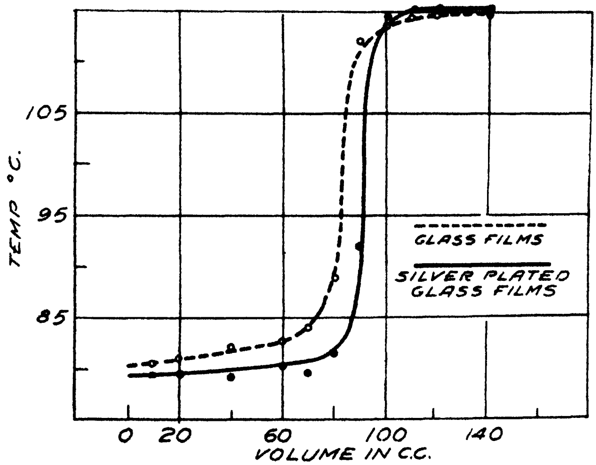

FIG. 12
Benzene and Pyridine

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[1] J. Ind. Eng. Chem., 14, 477 (1922).

No hint of anything of this sort appears in the book by Robinson,[1] also from the Massachusetts Institute of Technology. "It will be recalled that a fractionating column consists of a system up through which vapors are passing, and down through which a liquid is running, countercurrent to the vapor, the liquid and vapor being in more or less intimate contact with each other. Furthermore, the vapor and liquid should be in equilibrium with each other at any point in the column, the liquid and vapor at the bottom of the column being richer in the less volatile component than at the top. It is evident therefore that the action of such a column is similar to that of a scrubbing or washing column, where a vapor is removed from a gas which is passing up through the column, by bringing into contact with it, countercurrent, a liquid in which the vapor is soluble, and which will remove it from the gas."

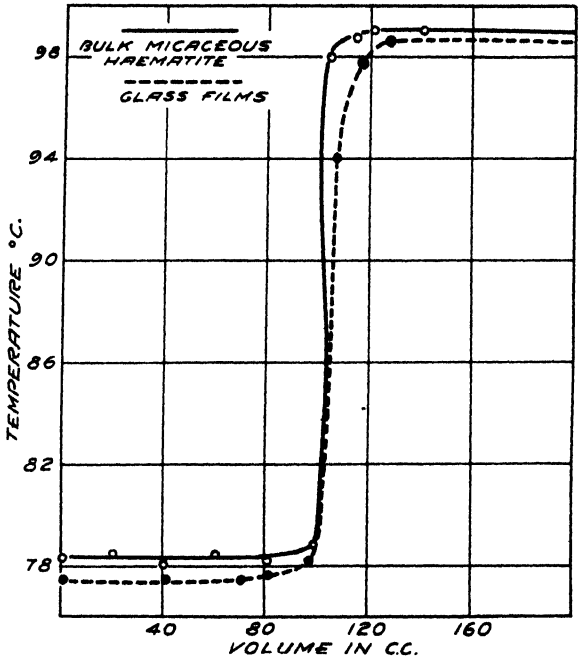

FIG. 13
Alcohol and Water

"In general, fractionating columns may be said to consist of cylindrical shells filled with distributing material which breaks the descending current of liquid up into thin streams and brings the ascending current of vapor into intimate contact with these streams. The earliest type of column, and one which is still used to a large extent, consists of a cylindrical shell filled with pieces of inert solids, usually small irregular pieces of stone, poreclain, coke, and other similar materials. This type of column is similar to the fractionating device which is used in the chemical laboratory, which consists of a glass cylinder filled with a large number of small glass beads. This type of column is inexpensive to construct and, for many purposes, will furnish sufficiently good fractionation. It, however, tends to form channels; that is, the vapor will tend to pass up through one portion of the cross-section of the column while the liquid may tend to descend through another portion of the cross-section, thus defeating the purpose of bringing the liquid and vapor into intimate contact with each other.

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[1] "The Elements of Fractional Distillation", 58, 83 (1930).

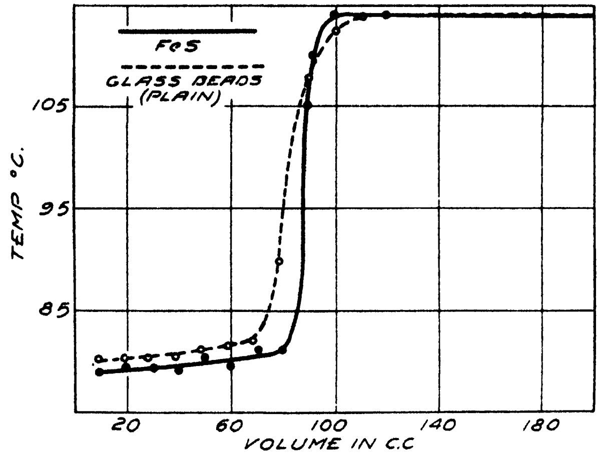

FIG. 14
Benzene and Pyridine

"In filled columns of this sort, channelling is, to a certain extent, overcome by using filling material of a uniform nature, such as specially-made stoneware shapes which, when carefully packed into the column by hand, insure even distribution of vapor and liquid. Such filled types of columns are frequently used in the distillation of acids such as nitric and sulphuric acid and are very successful for such purposes. It must be remembered, however, that even under the best circumstances, the contact between vapor and liquid in such columns is poor, and therefore they should be used only where it is a relatively simple matter to separate the more volatile from the less volatile component."

"Another variety of fractionating column of the filled type has for the filling material, small cylindrical rings or tubes, the length of each ring being equal to its diameter. These rings, which are known as Raschig rings from their inventor, are not packed carefully into the columns, but are dumped in, and owing to their dimensions and shape, form a fairly uniform packing with very little opportunity for liquids and gases to channel. They have the further advantage of offering a very large surface wet with liquid and exposed to the action of the vapor and there are no pockets where liquid may be caught and held from running down."

It seems probable that selective adsorption accounts for glass films being worse than carborundum or micaceous haematite with mixtures of benzene and pyridine, and better than micaceous haematite (and presumably carborundum) with mixtures of alcohol and water. It is known that water wets glass more readily than it does carborundum and that benzene and pyridine wet carborundum and micaceous haematite more readily than they wet glass. On this basis the better behavior of silver-plated glass films over plain glass films with benzene and pyridine would be due to the fact that the hydrocarbons wet metal more readily than they do glass. If this is a good working hypothesis, we should expect ferrous sulphide to make a good column filling for benzene and pyridine, even though it does not form flat plates or have sharp edges. The bubble flotation process for ores depends on the fact that the sulphide ores are adsorbed strongly by "oil" while the siliceous gangues are not.

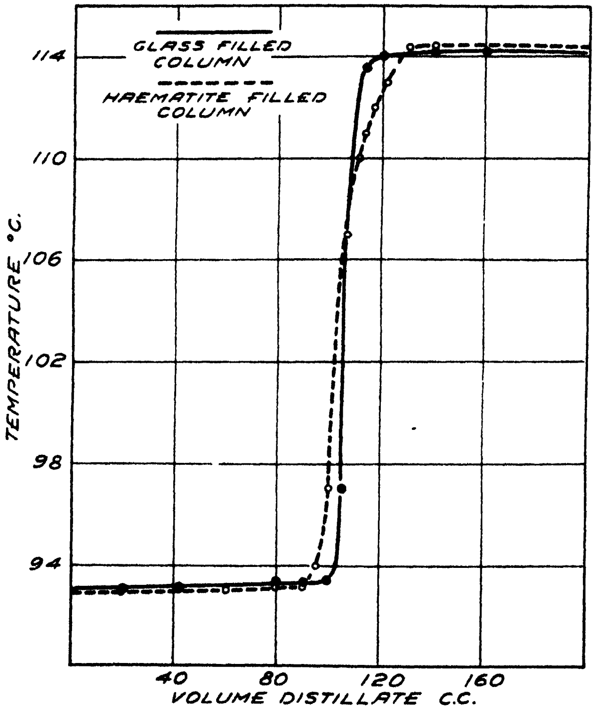

FIG. 15

Water and Pyridine

Excess of pyridine over the constant-boiling-mixture

Bulk ferrous sulphide was crushed to particles of somewhat larger size than the glass beads used in the check run. The results are shown in Fig. 14 and indicate that ferrous sulphide is much more satisfactory as a column filling than glass beads when one is fractionating benzene and pyridine.

The question of specific action is brought out even more clearly by some experiments with pyridine and water. There is a constant-boiling-mixture, which we will call CBM. It contains fifty-nine percent pyridine and boils at 93.2°. Experiments were made on the separation of the constant-boiling-mixture from pyridine and from water with glass beads and with micaceous haematite. The results are given in Figs. 15 and 16. When separating the constant-boiling-mixture from pyridine, glass Raschig rings are distinctly better than micaceous haematite. When separating the constant-boiling-mixture from water, micaceous haematite is distinctly better than glass rings.

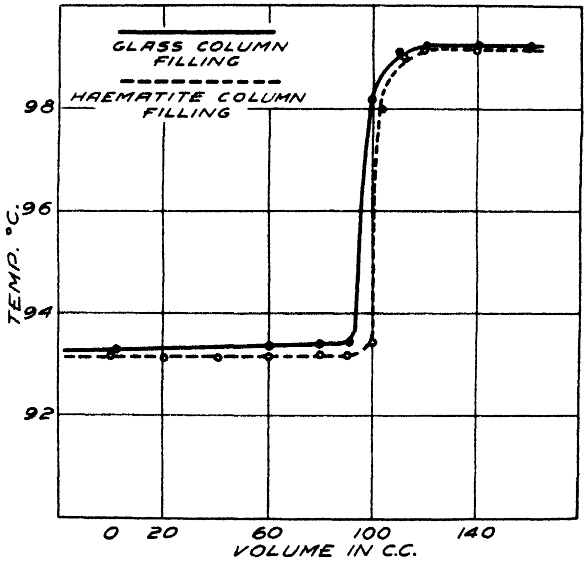

FIG. 16

Water and Pyridine
Excess of water over the constant-boiling-mixture

It seems, therefore, to be established that selective adsorption must be a factor in determining the efficiency of a fractionating column. The next question is how it probably acts. It is obvious that a column filling must adsorb the liquids, at least to the extent of being readily wetted by them. If they did not, the column filling would simply be so much dead space in the column and we would in effect be distilling through a narrow tube. One such experiment was tried using chloroform and alcohol, and distilling them through a column containing activated cocoanut charcoal. Chloroform vapor is only adsorbed very slightly by this charcoal but is readily adsorbed by glass. At the beginning of the distillation the charcoal remained perfectly dry and the liquid meniscus could be observed to climb up the glass wall of the distilling column.

Of course if the filling were of some porous adsorbing material, the liquid would be adsorbed so strongly that it could not pass down through the column as reflux or re-vaporise, and flooding would result. This happens if we try to use pumice or charcoal. If, however, the adsorption takes place only on the surface, the time of contact is increased, all of the surface is utilized, and the column therefore works well.

We have not yet considered the reflux or down-flowing portion of liquid rich in the volatile component. This is one of the most important factors in column operation. It is better distillation practice to obtain this reflux by condensing all of the vapor at the top of the column and returning a portion from this point, so that the reflux passing down the column is a maximum throughout the entire length of the column.[1] This practice is almost universal in the operation of large commercial stills; but is not ordinarily used in small laboratory columns. The latter depend upon condensation within the column to furnish the reflux. While this is not the best practice, it is less bad in a column which condenses the vapor readily by adsorbing it without making it necessary to distill very slowly.

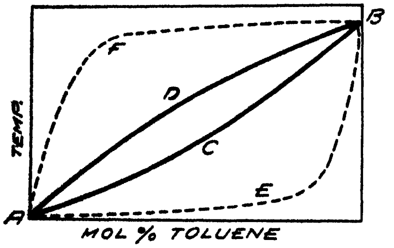

Fig. 17
Boiling-point Curves for Benzene and Toluene.

There are evidently two limiting possibilities in regard to selective adsorption by the column filling. There may be almost exclusive adsorption of the lower-boiling component or almost exclusive adsorption of the higher-boiling component. It is obvious that the first would be bad because that would lower the vapor pressure of the lower-boiling component and would therefore make fractional separation by distillation more difficult. At first sight it seems as though very strong adsorption of the higher-boiling component would be desirable and that view was held in this laboratory for a while. A more careful study of the situation showed the fallacy in the reasoning. If we could get practically exclusive adsorption of the higher-boiling component, there would be no need to do fractional distillation. We should then filter the solution through a sufficient mass of the adsorbent and draw off the lower-boiling component practically pure. If we did do fractional distillation, we should get a very effective separation at first, but after that, we should get no beneficial effect from the column filling.

It is thus evident that a good column filling should adsorb both components of the distilling mixture quite definitely and the problem is to define the ideal way in which the adsorption with varying composition of the distilling mixture. In Fig. 17 are shown the boiling-point curves for benzene and toluene as taken from Robinson.[2] The abscissas are molecular concentrations of the two liquids and the ordinates are temperatures when the pressure is one atmosphere. ACB is the liquidus curve and ADB the vapor composition curve. I have added two dotted lines showing hypothetical

[1] Robinson: "The Elements of Fractional Distillation," 83 (1930).

[2] "The Elements of Fractional Distillation," 41 (1930).

compositions of the adsorbed liquid films for the two limiting cases. AEB is the curve when the lower-boiling component is adsorbed almost exclusively and AFB is the curve when the higher-boiling component is adsorbed almost exclusively. The actual curves and also the ideal curve will lie somewhere between these limiting curves AEB and AFB. The moment the facts are presented in this way, it seems certain that the ideal adsorption curve would coincide with the liquid ACB, because the adsorption forces would be tending to produce a liquid film having exactly the same composition as the liquid in equilibrium with the vapor. In other words, an ideal column filling would adsorb the two components of any binary liquid mixture as is, without producing positive or negative adsorption.

It would take a good while to prove this point and the time at my disposal was unfortunately too short, so the study of the selective adsorption by solids from binary liquid mixtures has had to be postponed. Until that has been done, it does not seem profitable to discuss the question of plates versus needles in much detail. With thin plates there is more surface in proportion to the edges than in prismatic needles. Bancroft[1] has pointed out that "a plane will adsorb a certain amount of gas under standard conditions; but that two plane surfaces placed close together will adsorb a good deal more gas than the same surfaces would if each did not re-enforce the other and modify the concentration gradient". If, as seems probable, the condensation and evaporation take place at the edges, the liquid then spreading over the surface or being drawn from it, this might account for the phenomena observed.

The general results of this paper are as follows:—

1. Mr. Midgley's observations on fractional distillation have been confirmed and extended.

2. Other things being equal, thin plates are better as a column filling than needles.

3. The chemical nature, as well as the physical structure, of the column filling affects the curve for fractional distillation, the effect being specific.

4. With benzene and pyridine, carborundum and micaceous haematite are better than glass beads or silver-plated glass films.

5. Ferrous sulphide is better than glass with benzene and pyridine.

6. Needle ore (a form of haematite) is not good with benzene and pyridine; nor is a very fine carborundum.

7. With alcohol and water, glass is better than micaceous haematite.

8. Glass Raschig rings are better than micaceous haematite when separating the constant-boiling mixture of pyridine and water from excess of pyridine, and worse when separating this constant-boiling mixture from excess of water.

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[1] "Applied Colloid Chemistry", 7 (1926).

9. It is probable, though not yet proved, that the ideal adsorption curve for a column filling would coincide with the liquidus curve in the boiling-point diagram for that pair of liquids.

This problem was suggested by Mr. Thomas Midgley, Jr. and I thank him for his assistance in connection with it. The work has been done under the direction of Professor Bancroft who formulated the present theory of the phenomenon. I am indebted to the Carborundum Company and to the Norton Company for samples of carborundum and crystolon respectively. The two products behaved alike in the fractional distillation. I also wish to express my thanks to Miss Anna S. Nestmann for work done on the drawings.

Cornell University.

THE DESORPTION OF GASES FROM MOLECULARLY PLANE GLASS SURFACES[1]

BY JAMES ROWLAND CURRY[2]

Previous investigators[3] have shown that when non-aqueous vapors were adsorbed on molecularly plane glass surfaces the layer of adsorbed molecules was not more than of mono-molecular thickness. However, as Latham pointed out, the method used did not permit them to determine to just what extent the surface was covered and indeed did not prove definitely that under the conditions used the adsorption of a mono-molecular layer of vapor really did take place. Obviously it would be of interest to determine if there were adsorption and if so, to investigate how much and at what temperature desorption from the glass surface occurred.

In order to measure small amounts of adsorption or desorption it is necessary to measure the change in the pressure in a system that has a large ratio of surface to volume. Past investigators have achieved this experimental condition by using a very large surface, usually powdered glass, glass wool or cover glasses, and measuring the pressure change by means of a sensitive gauge. In all such methods the results are influenced by capillarity and besides there is some doubt as to the exact extent of the surface since in no case is the surface molecularly smooth. It was thought that a very simple apparatus could be designed in which there would be no doubt as to the condition and extent of the surface. It was believed that the best way to achieve this was to obtain a large ratio of surface to volume by using an adsorption bulb in which the volume was very small. In order to obtain this small volume, it was thought that the use of a fine capillary tube afforded the best way, but the use of such a tube would preclude the method used by the above investigators for the production of a molecularly plane surface, i.e., by blowing the bulb in a thoroughly melted piece of glass taking particular pains to exclude all moisture. However, the belief was held that if glass were kept for some time at a temperature somewhat below the temperature of definite softening the surface would become molecularly plane due to the action of the surface tension. Consequently preliminary work was done to find out whether or not this idea was correct.

Preliminary Work

The method used to determine if the surface was molecularly smooth was that of the above mentioned workers so it will not be described in detail. In principle it consists in measuring the pressure-temperature relationship of a vapor at its dew-point. If the intersection of the vapor pressure curve and the Charles law curve is a sharp angle, it indicates that there is no adsorption greater than a mono-molecular layer so the surface is assumed to be molecularly plane.

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[1] From the dissertation submitted to the Johns Hopkins University in partial fulfillment of requirements for the degree of Philosophy.

[2] Du Pont fellow in Chemistry.

[3] Frazer, Patrick and Smith: J. Phys. Chem., 31, 897 (1927); Latham: J. Am. Chem. Soc., 50, 2987 (1928).

The apparatus used was essentially like that of McHaffie and Lenher[1] so will not be described. The only difference was in the treatment of the bulb in which the measurements were made. In this case a piece of soda lime glass was obtained from the stock room and the dust carefully wiped out of it by means of cotton. Then it was washed with alcohol and one end sealed shut so as to form a cylinder. Care was taken not to heat any more of the glass than was absolutely necessary. This bulb was immersed in a Kjeldahl flask partially full of boiling sulfur so that its bottom was just above the surface of the sulfur. The bulb was connected to a trap and this latter to an oil pump. The trap was kept surrounded with solid carbon dioxide in order to keep oil vapors out of the bulb. The sulfur was kept boiling vigorously so that its vapors surrounded the bulb and a vacuum maintained for slightly over four hours. Then after cooling the pump was shut off and air let into the bulb through a tube containing P_2O_5. The bulb was then sealed to the rest of the apparatus and immediately pumped out.

The vapor used in the measurements was toluene which had been well deaerated. The pressure-temperature relationship was measured when the temperature was both rising and falling. A slight hysteresis was found but in both cases the intersections of the vapor pressure—Charles law curves were very sharp. From this it can be concluded that the surface of a fresh, unwashed, soft-glass tube is rendered molecularly plane by long heating at a temperature somewhat below its melting point.

Description of the Apparatus

The principle, upon which the determination of the amount of desorption was based, consisted in measuring the gas pressure, as the temperature was raised, in a fine capillary tube by means of an adjustable mercury manometer one side of which formed part of the capillary tube.

A diagram of the adsorption apparatus is given in Fig. 1. It consisted essentially of a 0.10 mm lead-glass capillary tube joined to a 1.0 mm capillary tube by means of a very square joint. Care was taken in making this joint to keep the larger capillary tube very uniform and the result was that mercury could move in it very uniformly and regularly up to 1.0 mm from the square joint. This uniformity also did away with capillary depression, so consequently the mercury stood at the same height in tube A and on the fine capillary side when the pressures above the two columns were the same. The tube leading from the cut-off connected to a leveling arrangement in which all rubber was eliminated. The mercury level in these two vertical tubes was adjusted by the movement of a solid glass rod dipping into the open end of the mercury reservoir. The height of the adsorption apparatus in relation to the leveling arrangement was such that when a vacuum existed in the apparatus the mercury meniscus was slightly below the cut-off.

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[1] McHaffie and Lenher: J. Chem. Soc., 127, 1559 (1925).

The tube A was connected by a soft glass to pyrex seal to traps and a pumping system consisting of a mercury diffusion pump backed up by a Hyvac oil pump. Between the mercury pump and the rest of the system there was a trap which was kept surrounded by solid carbon dioxide, principally to keep oil vapor out of the apparatus. The rest of the system consisted of a McLeod gauge and several bulbs and mercury traps which were used to de-aerate liquids. Between the two pumps there was a stop-cock for the purpose of introducing gases.

The furnace used to heat the apparatus consisted of an iron pipe covered with a layer of asbestos upon which nichrome wire was evenly wound and finally a thick layer of asbestos on the outside. It was arranged so that it could be readily slipped over and removed from the capillary tube and was also adjustable vertically above the zero point. The temperature of the furnace was measured by a chromel-alumel thermocouple connected to a portable potentiometer. The movement of the mercury meniscus was followed by means of a carefully leveled cathetometer capable of reading to 0.03 mm.

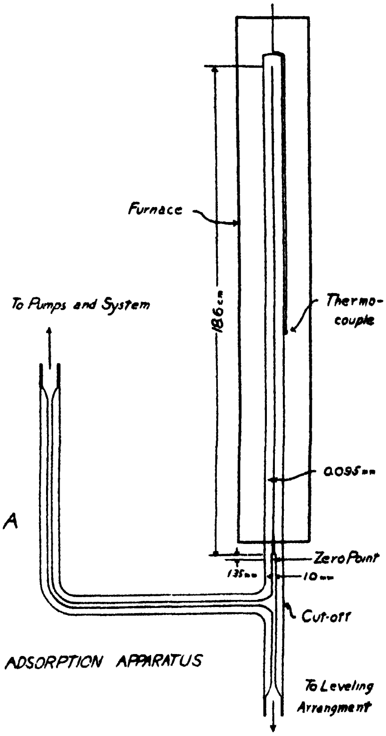

FIG. 1

From the dimensions of the apparatus it is seen that if the mercury is kept at the zero point the ratio of surface to volume in the fine capillary is about 200 and a rough calculation shows that if a mono-molecular layer of a gas is desorbed at 300°C while the volume is kept constant the pressure increase will be about 8 mm and this would be shown by a rise of this height in the mercury in tube A. Thus it is seen that the apparatus is quite sensitive to desorption.

The ratio could have been increased greatly by bringing the mercury up into the fine capillary tube; but preliminary work had shown that experimental difficulties prevented this procedure. In practice the bottom of the furnace was about 1.0 cm above the mercury meniscus at the zero point and under such conditions the vapor pressure of the mercury did not interfere seriously.

After the apparatus was completed it was sealed to the system and the furnace lowered as far as possible. It was then pumped out to a pressure of less than 10^{-6} mm and heated for two hours while the temperature rose gradually to 300°C, then during the next two hours the temperature was allowed to rise to 400°C. At this point the pumps were turned off and air allowed to enter the system through a tube containing P_2O_5. The temperature was kept between 400°C and 425°C for six hours and then the system allowed to cool slowly. The preliminary work had been with soda-lime glass and since the capillary tube was of lower melting lead glass it was thought that the above treatment was ample for the production of a molecularly plane surface and the results obtained later verified this. After this treatment great care was taken not to allow any moisture to get into the system.

The gases used, their source and method of drying are given below:

Carbon dioxide, hydrogen, ethylene and ammonia were obtained from iron tanks. The first three were dried by passing them through a tube filled with P_2O_5; the ammonia was passed through a tube of calcium oxide.

Carbon monoxide was made by dehydrating formic acid by means of concentrated sulfuric acid. It was passed through soda-lime and stored over water. Before it was allowed to enter the apparatus it was passed through a tube of P_2O_5.

The toluene was some that had been dried over P_2O_5 and was de-aerated until the partial pressure of air in it was less than 10^{-4} mm.

Experimental Procedure

The procedure followed in an experiment was the following. The adsorption apparatus was pumped out for several hours at 340°C by means of the diffusion pump and then allowed to cool with the pumps still in operation. When the temperature had fallen to about 75°C the pumps were shut off and in a short time the gas to be studied was allowed to enter the apparatus by means of the previously mentioned stop-cock until the pressure was about one atmosphere. Then the gas was pumped out until the pressure was less than 0.01 mm; this flushing-out process was repeated three times and the gas finally allowed to remain in the system at a pressure of 760 mm. The apparatus was allowed to stand in this condition for varying lengths of time and then pumped out for three-quarters of an hour by means of the oil pump alone. Sometimes the capillary tube was surrounded by solid carbon dioxide during the pumping-out period; when this procedure was used, the pump was not started until the cooling agent had been in position for twenty minutes and in addition the cooling mixture was adjusted so that a reading could be made while it was in place.

The manipulation of the apparatus was quite simple. After the pumping period was over, the mercury was raised above the cut-off (see Fig. 1) so that the meniscus came exactly to the zero point. From the dimensions of the apparatus it was calculated that due to compression the pressure in the capillary was 5.8 times what it was at the end of the pumping-out period. Under experimental conditions this pressure was about 0.10 mm when the meniscus was at the zero point. With the meniscus at the zero point the height of the meniscus in tube A, was read; then the mercury was lowered about one mm while the capillary tube was heated; then at various temperatures, after standing half an hour or longer, the meniscus was brought up to the zero point and the increase in height noted on the other side. Three readings were made at each temperature and the mean recorded; they checked within 0.10 mm.

The temperature was never raised much above 325°C due to the possibility of the capillary tube collapsing. In some cases after the last reading at the highest temperature the furnace was turned off but the mercury not lowered. Then a reading was taken in the morning and recorded.

Since part of the volume (that just above the mercury meniscus) was not in the furnace it was necessary to find its temperature for different furnace temperatures. This was done by putting a thermocouple in contact with the exposed portion and finding its temperature as that of the furnace was raised. These values were plotted to assist in the calculations. When the furnace temperature was 330°C the temperature of the exposed portion was 120°C.

Since the mercury at the zero point did not remain at room temperature it was necessary to run a blank in order to obtain the necessary corrections to apply to the readings observed when a gas was being desorbed. To do this the apparatus was given the usual preliminary pumping-out at 340°C and in addition was pumped out by means of the diffusion pump for two hours at room temperature before a reading was made. Then the usual readings were taken as the temperature was raised. When the temperature had reached 330°C the mercury was lowered and the apparatus thoroughly pumped out by means of the diffusion pump for an hour and a half and then the mercury raised and another reading taken. The two readings checked within 0.10 mm indicating that the slight pressure increase noticed had not been due to desorption of a gas. At 330°C the value of the blank was 0.45 mm. This blank experiment was made several times and the average values at the different temperatures plotted against the corresponding furnace temperatures.

Results

When the above procedure was followed the data given below were obtained.

TABLE I

No. 1: Air, 10 hrs. P.P. 0.011 mm.

Temp.	T. S.	O. R.	C. P.	m*
25°C	.5	0.06mm.	0.0mm.	0×10^{13}
100	.5	1.0	.85	6
235	.5	1.5	1.10	7
315	.5	1.8	1.25	7
315	1.0	1.9	1.35	7

TABLE I (Continued)

Temp.	T. S.	O. R.	C. P.	m*
No. 2: Carbon dioxide, 14 hrs. P.P. 0.011 mm.				
25°C	.5	0.07mm.	0.0mm.	0×10^{18}
120	.5	0.7	0.50	4
205	.75	1.7	1.35	9
290	.75	2.6	2.10	12
298	1.0	2.55	2.05	11
No. 3: Carbon dioxide, 35 hrs. P.P. 0.018 mm.				
25°C	.5	0.1mm.	0.0mm.	0×10^{18}
100	.5	0.9	0.7	5
190	.5	1.5	1.15	8
315	.75	2.25	1.65	9
315	2.75	2.90	2.30	12
310	4.0	2.90	2.30	12
No. 4: Toluene, at 27 mm. for 13 hrs. P.P. (0.017)				
25°C	.5	0.1mm	0.0mm.	0×10^{18}
105	.5	0.55	0.35	3
210	.75	1.35	0.95	6
315	.5	1.85	1.25	7
315	2.0	1.80	1.20	7
305	4.0	1.90	1.30	7
Morning		0.60	0.50	4
No. 5: Ammonia, 10 hrs. P.P. 0.02mm.				
25°C	.5	0.12mm.	0.0mm.	0×10^{18}
120	.75	1.6	1.35	10
212	1.5	1.95	1.55	10
325	1.5	2.45	1.80	10
No. 6: Ammonia, 17 hrs. P.P. 0.04 mm.				
25°C	.5	0.22mm.	0.0mm.	0×10^{18}
105	.5	1.5	1.15	9
220	.75	2.75	2.20	14
320	.75	2.95	2.15	12
No. 7: Hydrogen, 18 hrs. P.P. 0.008 mm.				
25°C	.5	0.05mm.	0.0mm.	0×10^{18}
120	.5	1.0	0.85	6
220	.75	1.45	1.1	7
320	.75	1.40	0.90	5
320	1.25	1.40	0.90	5

TABLE I (Continued)

No. 8: Hydrogen, 16 hrs. P.P. 0.02 mm.

Temp.	T. S.	O. R.	C. P.	m*
−78°C	.5	0.09mm.	0.0mm.	0×10^{18}
25	1.0	3.30	3.2	27
120	.5	5.8	5.55	40
215	.5	6.0	5.40	36
310	.75	6.15	5.55	32
Morning		2.20	2.10	18

No. 9: Hydrogen, 16 hrs. P.P. 0.036 mm.

−78°C	.5 hrs	0.15mm.	0.0mm.	0×10^{18}
25	1.5	2.9	2.7	23
200	.5	6.2	5.7	39
300	.5	6.3	5.6	33
340	1.0	5.7	4.9	27
Morning		1.9	1.7	14

No. 10: Hydrogen, 111 hrs. P.P. 0.007 mm.

−78°C	.5 hrs.	0.03mm.	0.0mm.	0×10^{18}
25	1.0	1.85	1.8	15
120	1.0	4.15	4.00	29
220	.5	5.4	5.1	33
325	.5	5.5	5.0	28
325	1.0	5.2	4.7	26
330	2.0	4.9	4.4	24
330	3.0	4.75	4.25	24
Morning		2.6	2.55	22

No. 11: Carbon Monoxide, 12 hrs. P.P. 0.006 mm.

−78°C	.5 hrs.	0.03mm.	0.0mm.	0×10^{18}
25	1.0	2.3	2.25	20
120	.5	3.4	3.25	24
200	.5	3.85	3.55	24
330	1.0	3.6	3.1	18
Morning		1.2	1.15	10

No. 12: Carbon Monoxide, 16 hrs. P.P. 0.007 mm.

−78°C	.5 hrs.	0.03mm.	0.0mm.	0×10^{18}
25	1.0	1.6	1.55	13
105	.5	3.15	3.00	23
200	.5	3.65	3.35	22
325	.1	4.35	3.85	22
325	.5	4.05	3.55	20
325	1.5	2.9	2.4	14

TABLE I (Continued)

No. 13: Carbon Monoxide, 68 hrs. P.P. 0.008 mm.

Temp.	T. S.	O. R.	C. P.	m*
−78°C	.5 hrs.	0.04mm.	0.0mm.	0×10^{18}
25	1.0	1.7	1.65	14
115	.5	3.7	3.55	25
200	.5	5.1	4.8	32
315	.5	5.6	5.1	29
315	1.5	4.4	3.9	23
315	2.0	3.5	2.15	18
Morning		2.2	2.15	18

No. 14: Ethylene, 15 hrs. P.P. 0.015 mm.

25°C	.5 hrs.	0.09mm.	0.0mm.	0×10^{18}
120	.5	0.9	0.7	5
205	.5	1.2	0.85	6
325	.75	1.35	0.75	4
325	1.5	1.3	0.7	4
Morning		0.3	0.3	2

No. 15: Ethylene, 15 hrs. P.P. 0.01 mm.

−78°C	.5 hrs.	0.06mm.	0.0mm.	0×10^{18}
25	1.0	1.45	1.4	12
130	1.0	2.6	2.4	17
200	1.0	3.2	2.9	19
320	.5	3.4	2.85	16
325	1.25	3.0	2.45	14
340	1.5	3.1	2.5	14
Morning		0.8	.75	6

The number of hours following the name of the gas in Table I gives the length of time that the gas was allowed to stand in the apparatus before it was pumped out. The value following P.P. indicates the pressure at the end of the pumping-out period, i.e. just before the mercury was raised above the cut-off. The temperature is that of the furnace. Where the initial temperature is −78°C it means that the capillary tube was surrounded by solid carbon dioxide while it was being pumped out and then a reading taken under those conditions. The figures under T.S. give the length of time in fractions of an hour that the furnace was kept at the temperature in question before a reading was taken. The values listed under the heading O.R. show the height in mm. that the mercury column rose while the temperature rose from the initial value to the value in question. The value for O.R. at the lowest temperature was obtained by multiplying P.P. by 5.8 (ratio of volumes before and after compression).

The rise observed in the mercury column in tube A as the temperature is increased is the result of three influences, (1) the increase in thermal pressure of the molecules present originally in the gas phase, (2) the change due to the increase of the vapor pressure of the mercury, (3) desorption of molecules and the increase in thermal pressure of molecules desorbed at lower temperatures.

The magnitude of (1) is small since the original pressure was always about 0.10 mm. and it can be calculated from the original pressure and the temperature of the exposed and covered parts of the adsorption apparatus. (2) is found from the results of the blank experiment. Applying these corrections the values listed under C.P. (corrected pressure) show the increase in pressure that is due to desorbed molecules. The next column, m*, gives the number of molecules which correspond to the pressures listed under C.P. and of course these figures give the total number of molecules that had been desorbed up to and including the temperature in question. The way m* increases shows the amount of desorption that takes place as the temperature is raised.

In order to calculate m* it was assumed that all the volume in the furnace was at the furnace temperature and all the exposed portion was at the temperature as determined by the thermocouple put in contact with it. This latter assumption is undoubtedly not quite correct but since this exposed volume occupied such a short length it is quite justifiable. Using these temperatures and the respective volumes as calculated from the dimensions of the capillary tube and the corrected pressures, m* was calculated for each temperature.

From the observed pressures and the size of the capillary tube a calculation shows that in some cases the mean free paths of the molecules are larger than the diameter of the tube and one might think that the phenomenon of thermal transpiration would cause a complication in the calculations. However, when this was calculated it was found that it would change m* by much less than the experimental error so it is not of any importance.

In order to calculate the precision of m* it is necessary to take into account the magnitude of the error in O.R., the blank, the temperature, the pressure of the molecules originally present and the volume of the adsorption apparatus. Estimating all these as fairly as possible it comes out that the percentage error in m* is 25% when C.P. is 1.0 mm., and 15% when C.P. is 2.0 mm. and for higher pressures it is 10%.

Discussion of Data

Since the way desorption took place for the individual gases is plainly shown by the way m* changed with temperature it will not be necessary to go into a detailed discussion of the results for each experiment. Consequently only the more important things will be mentioned for each gas and finally a summarizing table will be given.

Air.—Desorption was practically complete by 100°C and further heating at higher temperatures caused no more change. Of course from this experiment alone it is impossible to tell if nitrogen or oxygen was the desorbed gas. In the work presented here it was not planned to study mixtures and this experiment was made essentially for orienting purposes.

Carbon dioxide.—Desorption seemed to be continuous up to 300°C so there is nothing to indicate that the glass surface was free of carbon dioxide at that temperature. In the second experiment, where the gas had stood in the apparatus over twice as long, the desorption at the higher temperatures seemed to take place a little more slowly but the total amount desorbed at 300°C was the same in both cases. It should be noted that a final heating of four hours at this temperature caused no further change.

Toluene.—This had been allowed to stand in the apparatus at a pressure of 27 mm. Since P.P. could not be measured it was assumed to be of the magnitude of the other experiment, since the pumping was the same as usual. The desorption seemed to be gradual and even in amount up to 250°C where it was complete. Keeping the temperature at 300°C for six hours caused no change whatever. The morning reading, which of course was at 25°, indicated that not quite half the molecules had been re-adsorbed. This last point will be discussed later.

Ammonia.—For this gas the second experiment, for which the time of standing was slightly longer and the initial pressure slightly higher, showed that the maximum desorption took place at a higher temperature and was a little larger in amount than for the conditions of the first experiment.

Hydrogen.—The data and the summarizing table show the main features of interest. Of course when the capillary tube was surrounded with solid carbon dioxide the amount of desorption was larger. One striking thing, that first became noticeable with this gas, is that at the higher temperatures there was an actual decrease in the number of molecules present. That is, when the temperature was increased the pressure did not increase as much as it should, and indeed in some cases after standing some hours at a high temperature the pressure was actually less than it had been previously. Since this phenomenon was encountered with other gases its explanation will be postponed until later. In some cases the desorption seemed to be reversible but it was not at all clean cut. In this connection it must be remembered that the morning reading was always at 25°. The results obtained when hydrogen was allowed to remain in the apparatus seven times as long as usual showed that, although the maximum desorption was slightly changed, there was no great difference in the behavior.

Carbon monoxide.—There is nothing in particular to be emphasized here. Long standing seemed to raise the minimum temperature and the amount of maximum desorption as well as to decrease the reversibility somewhat.

Ethylene.—The only unusual point to be noted here is that at the higher temperatures there was a decrease in pressure at first but on long standing it came to a constant value.

For purposes of comparison and for recapitulation of the above statements Table II has been compiled.

TABLE II

Temp. of 25°C

Exp.	14	1	7	4	5	6	2	3
Gas	C_2H_4	Air	H_2	C_7H_8	NH_3	NH_3	CO_2	CO_2
S.	15 hrs	10	18	13	10	17	14	35
P. P.	.015mm.	.011	.008	.017	.020	.040	.001	.018
M. T.	205°C	150	150	250	120	220	300*	300*
M. M.	6×10^{13}	7	7	7	10	13	12	12
F.	.32	.20	.20	.48	.24	.31	.36	.36

Temp. of −78°C

Exp.	15	12	11	13	10	9	8
Gas	C_2H_4	CO	CO	CO	H_2	H_2	H_2
S.	15 hrs	16	16	68	111	16	16
P. P.	.010mm.	.007	.006	.008	.007	.036	.020
M. T.	200°C	105	120	200	220	200	120
M. M.	19×10^{13}	23	24	32	33	39	40
F.	1.0	.76	.80	1.0	.94	1.1	1.1

T.S and P.P. have the same meanings as before. M.T. (minimum temperature) refers to the lowest temperature at which desorption was complete. M.M. refers to the maximum number of molecules that have been desorbed up to this temperature. F. refers to the fraction of the surface covered by the molecules desorbed.

In calculating this latter quantity, it was assumed that the desorbed molecules came exclusively from the surface that was entirely in the furnace, this had a magnitude of 0.55 sq. cm. and is 86% of the total possible area. Undoubtedly there was some desorption from the exposed surface but using the above assumption the value calculated will be the maximum possible. The diameter, or sphere of influence, of an adsorbed molecule was calculated from the density of the substances in the liquid state as given in the International Critical Tables. Since the densities are not available for all the substances at 25° and −78° one should not put too much weight on the absolute values listed under F. They only show the order of magnitude and the point to be emphasized is that even taking into account the above mentioned uncertainties there was no evidence that the layer of adsorbed molecules was of polymolecular thickness.

From the table the most striking thing is that for all the gases except carbon dioxide desorption was complete at fairly low temperatures. In some cases this minimum temperature was less than 120° and in only one was it over 220° and this was somewhat doubtful. It should also be added that desorption seemed to take place rather slowly at room temperature but when the temperature was above 150° it took place within about half an hour as a rule.

It appeared that a long saturation period had a slight effect on the subsequent desorption but it varied with the gas. The change was not striking enough to warrant any discussion.

In general, all that can be said as to the reversibility of the desorption is that the apparatus used did not permit careful study. The difficulty is that the conditions under which re-adsorption took place were quite different from the initial conditions of adsorption, particularly in regard to pressure, so one can not really say much about this.

From the data it will be noted that the gases which showed a decrease when kept for some time at the higher pressures were hydrogen, carbon monoxide, and ethylene but this behavior was not noticed with toluene or carbon dioxide. The decrease seemed to be of larger magnitude the higher the temperature and pressure and as mentioned before on very long standing at the higher temperatures it stopped entirely.

There seem to be only two reasonable explanations for this. The first is that at the higher temperatures the glass becomes permeable to some of the gases. This behavior has been well established experimentally but in this case there is no apparent reason why the decrease should finally stop as it did with ethylene. The other suggestion is that at the higher temperatures the mercury becomes permeable to some of the gases. Although this at first seems rather novel there is nothing known either from the standpoint of the properties of mercury or the results obtained with the above gases that is in conflict with this hypothesis. On the other hand there is no positive evidence as yet that mercury does behave in this way.

The above results on the desorption of gases are in accordance with the observations of Sherwood[1] who found that if glass was previously well annealed and then allowed to stand in the atmosphere for some time the gases given off when it was heated again to a temperature slightly below the annealing temperature were true adsorption products and corresponded roughly to a mono-molecular layer. In the above work the temperature never was raised above the preliminary annealing temperature and from the results of the experiments and the blank determinations there was nothing to indicate that there were any gases coming from the decomposition of the glass itself.

Experiments and Results with Water-treated Surfaces

All the work described above has been done in connection with glass surfaces that were molecularly plane and from which moisture had been carefully excluded. Naturally it would be of interest to obtain data on the desorption of water and also to see to what extent the surface of the glass was changed by contact with water vapor. Accordingly experiments were made to determine these points.

In order to do this the adsorption apparatus was allowed to remain for several days open to a bulb of water that had been sealed into the system.

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[1] Sherwood: Phys. Rev., **12**, 448 (1918); J. Am. Chem. Soc., **40**, 1645 (1918).

The vapor pressure was that of water at the temperature of the room and was about 25 mm. After this period the adsorption apparatus was pumped out for an hour and a half at room temperature by means of the oil pump and during this time the rest of the system was thoroughly out-gassed by means of a hand-torch. Then an experiment was made in the usual manner and the following data obtained.

No. 16	Water, 62 hours		P.P. (0.017mm)	
Temp.	T. S.	O. R.	C. P.	m*
25°C	.5 hrs	0.10mm	0.00mm	0×10^{13}
110	.4	9.75	9.55	72
210	.15	23.65	23.65	159

It is evident from these figures that water vapor is adsorbed strongly compared to the other gases and vapors used; undoubtedly a change in surface and mechanism of adsorption played an important role in this case.

After the last reading at 210° the apparatus was opened to the diffusion pump for ten minutes; then the furnace was turned off but the pump kept in operation. In an hour when the temperature had fallen to 65° the mercury was raised and a reading taken. Then the furnace was heated to 210° and in fifteen minutes another reading taken. The increase amounted only to 0.40 mm and indicated that practically all the water vapor desorbable at this temperature had been desorbed. The adsorption apparatus was then opened to the diffusion pump and the furnace turned off. When it had cooled to 65° it was opened to the bulb of toluene and flushed out in the usual way. The following results were then obtained.

No. 17	Toluene, 16 hours		P.P. (0.017mm)	
Temp.	T. S.	O. R.	C. P.	m*
25°C	.5 hrs	0.10mm	0.0mm	0×10^{13}
90	.15	0.90	0.75	7
135	.25	1.10	0.85	6
200	.33	5.15	4.80	33

This experiment was identical in all respects to that made before with toluene (No. 4) when the surface was molecularly plane. It will be seen that in this case the desorption up to 120° was slightly higher than that obtained before with toluene, in magnitude it was about the same as that of the previous maximum desorption. From this point on the desorption was very large so the value at 200° was over four times that of the other toluene experiment. It should be noted that the maximum temperature here was slightly lower than the maximum used in the water experiment. This, together with the check made after the previous experiment and the exhaustive pumping would indicate that this large desorption was due to toluene and not to additional water.

After this experiment the system was pumped out and a blank made and then dry hydrogen introduced as usual and the following results obtained.

No. 18 Hydrogen, 17 hours P.P. 0.007 mm

Temp.	T. S.	O. R.	C. P.	m*
25°C	.5 hrs	0.13mm	0.0mm	0×10^{18}
110	.15	0.45	0.30	2
200	.33	2.7	2.4	14
300	.33	12.7	11.55	69

This experiment was identical with the first one made on hydrogen (No. 7) except for the intervening water treatment. In this case the desorption at 200° was three times greater than it had been in the previous hydrogen experiment and from the considerations mentioned it is believed that this desorption corresponded to hydrogen and not to water vapor or toluene. In order to see what would happen when the temperature was raised above the maximum attained up to this point it was increased to 300°. The desorption occurring in this interval was very large, in all probability it was mostly water, but perhaps some toluene and hydrogen.

After the last reading at 300° the apparatus was pumped out for half an hour by means of the diffusion pump and then allowed to cool with pumping and again filled with hydrogen.

No. 19 Hydrogen, 17 hrs P.P. 0.007 mm

Temp.	T. S.	O. R.	C. P.	m*
25°C	.5 hrs	0.03mm	0.0mm	0×10^{13}
125	.15	0.35	0.15	1
190	.25	0.65	0.40	3
290	.25	1.65	1.20	10
325	.25	4.5	3.60	22

From this experiment it is seen that the desorption up to 200° is much smaller than in the preceding experiment; this is the interval in which the desorbed gas is in all probability hydrogen. In the last three experiments the temperature had never been raised higher than 300° and it is interesting to note that raising it in this experiment to 325° brought about quite a noticeable amount of desorption considering the small temperature interval, this was undoubtedly mostly due to the desorption of water.

By a comparison of the data obtained before and after the surface had come in contact with water vapor the following conclusions seem legitimate.

The water vapor itself is strongly adsorbed and comes off continuously while the temperature is being increased. A second heating through the same temperature range causes no further desorption but heating above the previous maximum temperature brings about more desorption.

After standing in contact with water vapor the glass showed a distinct but not enormous change in surface. Both toluene and hydrogen were adsorbed to about three times the amount on such a surface as on a molecularly plane surface and the desorption did not take place so readily. However, after additional experiments the amount of desorption diminished, which indicated that the surface was tending to become more and more molecularly plane. This points toward the action of water vapor alone as not being very drastic. It was consideration of this last point that led to the procedure of keeping the apparatus at a high temperature for only a short time. It is not to be expected that water vapor alone would dissolve out part of the glass and change the surface as much as treatment with cleaning solution and subsequent washing with water.

The author wishes to express his appreciation to Professor J. C. W. Frazer and Professor W. A. Patrick for suggesting the problem to him and also for advice during the pursuance of the work.

Summary

A simple apparatus has been designed for measuring the desorption of gases from glass surfaces. Its unique features are a very large ratio of surface to volume and the possibility of rendering its surface molecularly plane.

With the surface molecularly plane desorption measurements were made at −78°C and 25°C with the following gases, air, carbon dioxide, toluene vapor, ammonia, hydrogen, carbon monoxide and ethylene.

Measurements were also made after the glass surface had come in contact with water vapor.

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SOME PHYSICO-CHEMICAL PROPERTIES OF GUM ARABIC-WATER SYSTEMS AND THEIR INTERPRETATION

BY ROBERT TAFT AND LLOYD E. MALM

Water and gum arabic form systems which are generally regarded as colloidal systems, forming typical hydrophilic sols; or, at least, they are cited as examples of this class of systems in a number of text books of colloid chemistry.[1] Kruyt and Tendeloo[2] have in particular emphasized the lyophilic character of gum arabic and from viscosity studies upon gum arabic-water systems in the presence of electrolytes conclude that "gum arabic sols show the typical properties of a lyophilic colloid."

On the other hand, Thomas and Murray[3] have recently submitted evidence that these systems have some properties which resemble those of electrolytic solutions. These investigators showed that the metal-free material obtained from the electrodialysis of the commercial gum was an acid, possessing definite titration value with bases, and that the water solution of this material possessed a high osmotic pressure. This substance was therefore called arabic acid. The preparation of this material involved treatment with acids and precipitation by alcohol from water solutions of the original material. Carefully selected gum arabic without the acid treatment yields approximately 3% ash which O'Sullivan[4] showed to be chiefly calcium and magnesium carbonates. O'Sullivan considers this ash to be present in the original gum either as these metals in combination or as adsorbed salts. Apparently from the results of Thomas and Murray this mineral matter can be accounted for by assuming gum arabic to be a mixture of calcium and magnesium arabates.

We have determined a number of the physical properties of gum arabic-water systems in the hope that additional evidence for one or the other point of view as stated above could be found. The determinations were made upon purified gum; but the purification did not involve electrodialysis or precipitation with acid and hence the substance was not arabic acid but a supposed mixture of the calcium and magnesium salts of this acid. The properties determined were viscosities and densities over a considerable range of temperatures and concentrations, and in the presence of added electrolytes; freezing points up to a weight concentration of forty-five per cent; electrical conductance as a function of concentration at 30°C; and the hydrogen ion concentration of such systems.

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[1] A few examples are given herewith: Hatschek: "Physics and Chemistry of Colloids," 82 (1926); Zsigmondy, Spear: "Chemistry of Colloids," 24 (1917); Freundlich, Hatfield: "Colloid and Capillary Chemistry," 596 (1922).

[2] Kolloidchem. Beihefte, **29**, 396 (1929).

[3] J. Phys. Chem., **32**, 677 (1928).

[4] J. Chem. Soc., **42**, 1322 (1882).

Purification of Material

The gum arabic used was a commercial product described as "first grade tears." It was composed of small tear-like pieces, some of which were nearly colorless, while others were yellow. A small number of dark red to brown particles were distributed throughout the gum. In order to obtain a uniform product for examination a large quantity of the gum was dissolved in as little water as possible. This amounted to about twice as many cubic centimeters of water as there were grams of gum employed. This viscous solution was filtered under pressure and a clear colorless filtrate obtained. The acacia was then precipitated by the addition of ethyl alcohol. A sticky, white precipitate was obtained which was repeatedly washed with alcohol. It was then drained, pressed as free from alcohol as possible, and dried at room temperature. The product was then ground to a powder, placed in a long tube and a stream of dry air passed over it until it no longer had the slightest odor of alcohol. It was kept in this dry condition in desiccators containing calcium chloride and concentrated sulfuric acid. The dried product was a pure white powder, more dilute solutions of which were colorless. The more concentrated ones possessed a slight yellow color.

According to O'Sullivan, purification by this process in not too dilute solutions gives a product which is unaltered from its original state; i.e. no hydrolysis or other chemical changes have taken place.

Purification of two samples by this method gave specimens, 5% solutions of which, possessed identical densities and viscosities. A third sample purified by another observer gave a 5% solution possessing a viscosity approximately 2% lower than the above pair. This deviation was traced to insufficient drying and the sample was found to contain about 10% moisture. The supply of material used contained 0.87% moisture as determined by heating to 85° until constant weight was obtained. The original gum contained 10.5% moisture by this same procedure. When ignited and the ash content determined, two samples gave (dry basis)

I	3.05% Ash
II	3.07% Ash

Melting point determinations were attempted but the material charred between 190° and 200°C.

Viscosity and Density Determinations

A. Viscosity as a Function of Concentration.

There is very little published data upon the viscosity of gum arabic solutions, especially in the more concentrated systems. Much of the data that is given is stated without specifications of the method of purification, of the temperature at which the determinations were made or of the pH of the solutions. Went[1] has determined the viscosity of gum arabic solutions up to concentrations of 6% at different temperatures and pH values but in most cases takes no account of the effect of electrolytes which were added. H. Walter[1] has investigated the viscosities of such systems up to 12% at various temperatures, but the concentrations of many of her solutions were not determined directly.

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[1] Am. J. Physiol., 85, 458 (1928).

Our determinations of viscosity were made with two Ostwald pipettes. One of these viscosimeters required approximately 85 seconds for the flow of 5.32 cc of water through its capillary at 30°. The radius and the length of this capillary were determined by a measuring engine and found to be 0.087 cm. and 7.64 cm. respectively. The second viscosimeter had a volume of 1.84 cc, a capillary length of 7.91 cm. It is referred to below as the 20-second viscosimeter. The liquids were allowed to flow through these viscosimeters under their own hydrostatic head and consequently the kinetic energy correction was negligible and not applied.

The viscosimeters were calibrated by means of twenty, forty, and sixty weight per cent sucrose solutions as these solutions had viscosities which covered nearly the whole range of viscosities obtained for the gum arabic-water systems. The data for the absolute viscosities and densities of the sugar solutions were obtained from the International Critical Tables and Landolt-Börnstein Tabellen (1929) respectively.

Determination of the density and time of outflow were then made for the gum solutions and for the time of outflow of the sugar solutions. The absolute viscosities of the gum solutions were then computed from the usual relation

$$\eta_{\mathrm{gum}} = \eta_s \times \frac{D_g \times t_g}{D_s \times t_s}$$

where the subscripts g and s refer to the gum and sugar solutions respectively.

A stop-watch reading to 0.1 second was used for determining the times of outflow. The time in most cases could be checked to within 0.1 seconds but in the most concentrated ones deviations as high as 0.5 seconds were encountered.

The densities were determined in a 25 cc narrow necked flask fitted with a glass stopper. The flask was calibrated with water, using ICT data for the densities of water at the various temperatures. The volume could be adjusted to within 0.02 cc and consequently results are expressed with four significant figures.

Two automatically-regulated constant-temperature baths were employed for the determinations at 30° and 45°. Maximum temperature variations on these baths were ±0.01°C and ±0.03°C respectively. The measurements at 0°C were made in a clear three-liter Dewar flask filled with chipped ice and water, the top being carefully insulated. The temperature was checked with a certified thermometer and lay between 0.00° and 0.03°C during the determinations. To secure constant temperature at 15°C a four-liter beaker was filled with water at approximately 15° and the temperature was held to within 0.05° by hand regulation of the flow of cold tap water through a coil placed along the walls of the beaker.

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[1] Sitzungsber. Akad. Wiss. Wien., 129 IIa, 709 (1920).

The pH determinations in this and subsequent series of measurements, were made by the use of a quinhydrone electrode and a saturated calomel electrode at 25°. The potentials of the cells were measured by Leeds and Northup student potentiometer balanced by means of a certified standard cell. The pH values were computed from the expression

$$\mathrm{pH} = \frac{0.6992 - 0.2458 - E_c}{.0591}$$

where E_c is the measured cell potential, 0.6992 the electrode potential of the quinhydrone electrode at unit hydrogen ion concentration, 0.2458 the value assigned to the saturated calomel electrode and 0.0591 the value of the thermodynamic function 2.30 log RT/F at 25°C.

The data obtained at 30°C for various concentrations of gum arabic up to approximately 35 weight per cent are tabulated in Table I and the relative viscosities are shown graphically in Fig. 1.

TABLE I

The Viscosities of Gum Arabic Solutions at 30°C

pH of all solutions = 7.14 ± .02

	Wt. %	Density	Effective Density	Time	η_s/η_{sug}	η_s	η_s/η_{H_2O}
1.	1.22	1.000	1.610	37.0	0.985	.0132	1.65
2.	2.10	1 003	1.593	47.8	1.06	.0160	2.00
3.	2.70	1.006	1.607	51.4	1.22	.0184	2.30
4.	3.85	1.010	1.600	238.9	1.55	.0234	2.92
5.	3.95	1.011	1.599	65.2	1.56	.0235	2.93
6.	4.77	1.014	1.606	263.4	1.71	.0259	3.23
7.	5.54	1.017	1.608	79.2	.653	.0287	3.59
8.	7.33	1.024	1.595	106.8	.887	.0390	4.87
9.	8.55	1.029	1.604	120.0	1.00	.0440	5.50
10.	11.73	1.042	1.601	190.4	1.60	.0707	8.84
11.	15.68	1.050	1.604	256.1	2.18	.0959	11.9
12.	16.48	1.062	1.599	370.1	3.18	.140	17.5
13.	18.69	1.071	1.597	498.3	4.33	.190	23.7
14.	34.92	1.141	1.568	6070.0	7.08	2.41	300.

η_s is the absolute viscosity of the gum arabic solution. η_{sug} that of the sucrose solution used in the calibration of the pipette. η_s/η_{H_2O} is the relative viscosity of the gum arabic solution compared to that of water at 30°C. The effective density tabulated is a quantity which will be referred to later. Trials 4 and 6 were run with the 80 second viscosimeter. The 20% sucrose solution was used as the standard for trials 1 to 6 inclusive; the 40% sucrose solution for No. 7 to 13 and the 60% sucrose solution for No. 14.

The small diagram on the right of Fig. 1 is drawn with larger units of ordinates and abscissae in order to show the relative viscosity for the highest concentration of gum arabic used.

B. Viscosity as a Function of Temperature.

Determinations on the viscosities of two gum-arabic solutions were made at the temperatures of 0°, 15°, 30°, and 45° C. The concentrations of these two solutions were 3.84 weight per cent and 9.09 weight per cent respectively. Data for the first solution are given in Table II and that for the more concentrated one in Table III.

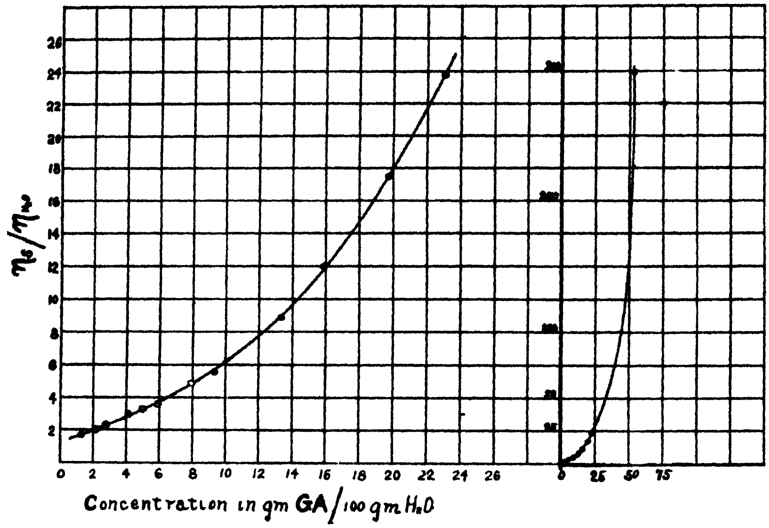

FIG. 1
Relative viscosity as a function of concentration at 30°C.

TABLE II
Concentration Gum Arabic, 3.84%

Temp.	D_s	Time	η_s/η_{H_2O}	η_s	Temp. Coeff.
0°	1 019	573	3 38	.0605	
15°	1.018	348	3.13	.0357	3.44
30°	1.101	239	2.93	.0234	2.76
45°	1.009	175	2.74	.0170	2.14

TABLE III
Concentration Gum Arabic, 9.09%

Temp.	D_s	Time	η_s/η_{H_2O}	η_s	Temp. Coeff.
0	1.197	1197	7.17	.128	
15	1.034	719	6.57	.0749	3.52
30	1.031	480	5.97	.0478	2.94
45	1.025	344	5.48	.0327	2.55

The relative viscosities as functions of temperature are shown graphically in Fig. 2, Curve 1, being that of the more dilute solution. The temperature coefficients tabulated in Tables II and III are in reality the average percentage decreases of viscosity per degree for each 15° interval and were computed from the relation

$$\text{Temp. Coeff.} = \frac{\eta t_1 - \eta t_2}{15} \times \frac{200}{\eta_2 + \eta_1}$$

C. Viscosity as Functions of Heat Treatment, Mechanical Treatment and Age.

Table IV shows the effect of heat treatment upon the viscosity of a gum arabic solution containing 5 grams of gum arabic in 100 grams of water. The solution was prepared at 25°, then placed in the constant temperature bath and its viscosity determined. Another portion of the solution was heated in a closed container on a water bath at 60° for one hour and then recooled to 30° and its viscosity determined. Similar treatment was given the solution at 80° and 95° for different lengths of time.

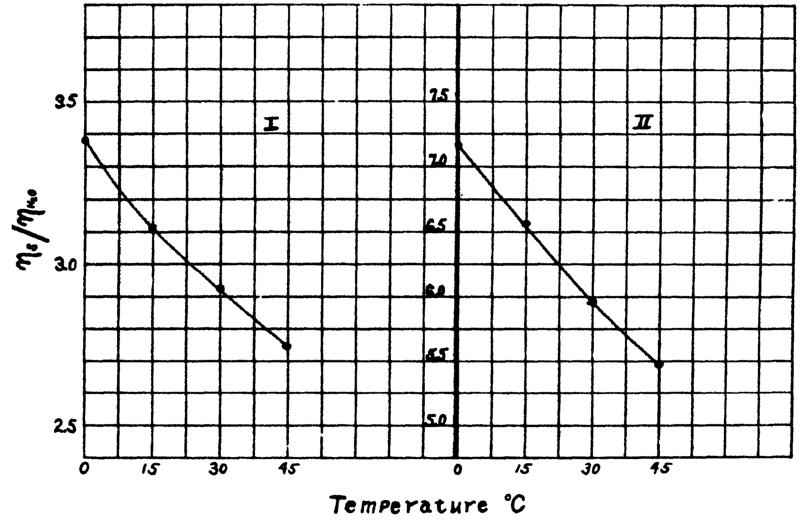

FIG. 2
Relative Viscosity and Temperature
Curve I–3.84% gum arabic; Curve II–9.09% gum arabic.

TABLE IV
5 grams Gum Arabic in 100 gms. of Water, 30°C

	D	T	η_s/η_{H_2O}	η_s
Orig. Sample	1.014	72	3.23	.0259
60°—1 hour	1.014	71	3.20	.0257
80°—4 hours	1.014	67.5	3.05	.0244
95°—6 hours	1.014	52.2	2.36	.0189

To determine the effect of mechanical treatment a solution of gum arabic similar to that described above was drawn thru the capillary of the viscometer and rapidly expelled some twenty times. The time of outflow was then determined and found to be unchanged as compared to that of the untreated sample.

Measurements of the variation of viscosity with age are limited as to length of time because bacterial action sets in from 36 to 48 hours after the solutions are made up. After several weeks the growth produced as a result of this action was present as large slimy lumps and the solutions had a sour smell. The more concentrated solutions did not show this phenomena until a much longer period had elapsed. The pH value of a 5% solution decreased by approximately six per cent in a period of several months. Keeping the solutions on ice very much retarded the formation of the growth.

Viscosity measurements on solution for different periods of time up to the appearance of the growth gave the same viscosities for solutions of the same concentration and temperature.

D. Viscosity as Function of Neutral Salt Content.

The viscosities of a solution of 5 grams of gum arabic in 100 grams of water were determined in the presence of a number of neutral salts, the concentration of the salt being made equal to 0.1 molal. The data is recorded in Table V, the temperature of measurement being 30°C. η_e and η_w represent the absolute viscosities of electrolyte solutions and of water respectively.

TABLE V

Effect of Various Sodium Salts upon the Viscosity of a Solution containing 5 grams of Gum Arabic in 100 grams of water at 30°C

Salt	Density	Time of Outflow	η_e/η_w	$\frac{\eta_{s+e}}{\eta_{sugar}}$	$\frac{\eta_{s+e}}{\eta_{water}}$	$\frac{\eta_{s+e}}{\eta_{elec}}$	η_{s+e}
NaF	1.016	180.0	1.014*	1.17_2	2.21_2	2.18	.0177
Na_2SO_4	1.026	48.8_7	1.041_3	1.20_7	2.27_8	2.18_8	.0182
NaCl	1.017	180.5	1.009_5	1.17_6	2.21_9	2.19_8	.0178
NaBr	1.023	181.0	1.005_3	1.18_7	2.23_9	2.22_7	.0179
$NaNO_3$	1.018	181.7	1.005_3	1.18_5	2.237	2.22_5	.0179
NaI	1.024	179.4	$.997_5$	1.17_7	2.22_2	2.22_7	.0178
NaSCN	1.017	181	$.997_6$*	1.17_9	2.22_5	2.23	.0178
Orig. Solution	1.014		1	1.71_2	3.23_0		

* The data for the relative viscosity of sodium fluoride and of sodium thiocyanate were determined in this laboratory, but the remaining data were obtained from the International Critical Tables, Volume V, page 15. The determination using sodium sulphate was run with the 20 second viscosimeter.

E. Viscosity as a Function of Calcium Chloride Content.

The effect of progressive additions of calcium chloride up to four gram equivalents per 1,000 grams of water upon the viscosity of a solution of gum arabic containing 5 grams of gum arabic to 100 grams of water was also determined. The observations were carried out at 30° and are tabulated below and shown graphically in Fig. 3, the abscissae representing the concentration of the electrolyte.

TABLE VI

Effect of Addition of Calcium Chloride on Viscosity of a Solution containing 5 gm. Gum Arabic in 100 gms. of Water. Temperature 30°C. pH of all solutions lie between 7.33 and 7.36

Equiv. per 1000 gms. of water	Density	Time	η_e/η_w	$\frac{\eta_s+e}{\eta_{sugar}}$	$\frac{\eta_s+e}{\eta_{water}}$	η_s+e/η_e	η_s+e
0.000	1.014	263.4	1.00	1.71	3.23		.0259
0.002	1.013	239.5	1.00	1.55	2.93	2.93	.0235
0.02	1.014	190.4	1.00	1.24	2.33	2.32	.0187
0.10	1.018	170.0	1.01	1.11	2.09	2.06	.0167
0.20	1.022	168.7	1.03	1.10	2.09	2.02	.0167
0.50	1.034	173.0	1.08	1.15	2.16	2.01	.0173
1.00	1.056	180.0	1.16	1.22	2.30	1.98	.0184
2.00	1.096	198.2	1.35	1.39	2.63	1.95	.0210
3.00	1.113	216.5	1.57	1.57	2.96	1.88	.0237
4.00	1.167	242.6	1.80	1.81	3.42	1.91	.0274

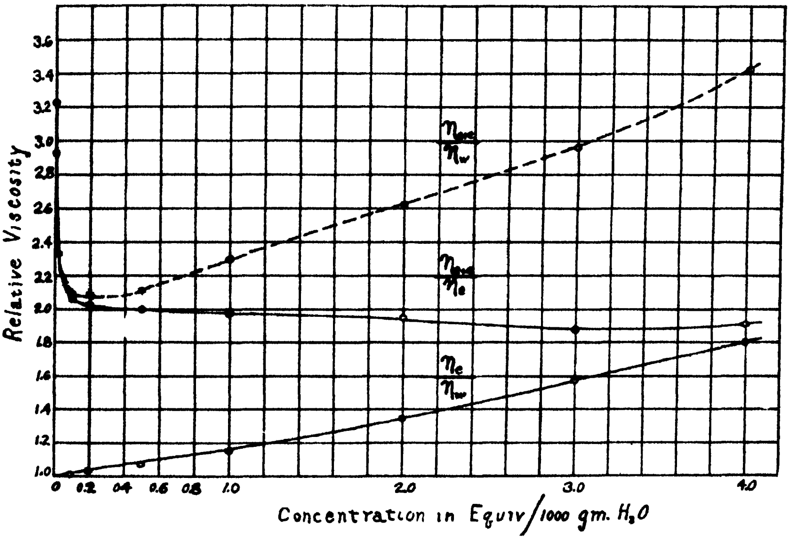

FIG. 3

Relative Viscosity as a function of calcium chloride content, $\frac{\eta_s + e}{\eta_e}$. There is also shown the ratio of the viscosity of the system to that of water, $\frac{\eta_s + e}{\eta_w}$, and the relative viscosity of calcium, $\frac{\eta_e}{\eta_w}$

The symbols have the same meaning as given previously. The data for η_e/η_w was obtained from the International Critical Tables (Vol. 5, p. 15), interpolation being made for those values not stated directly. The pH of all solutions containing the gum arabic was practically constant, lying between the limits of 7.33 and 7.36.

Freezing Point Determinations

The freezing points were determined in the ordinary way by the aid of a Beckmann thermometer up to weight concentration of 17%. Relatively sharp freezing points could be obtained from these solutions which were reproducible to 0.005 of a degree. For the more concentrated solutions a thermometer graduated in 0.1° was used. Here the precision of measurement was considerably less due to the very high viscosity of the solutions. The data obtained are given in Table VII and graphically in Fig. 4.

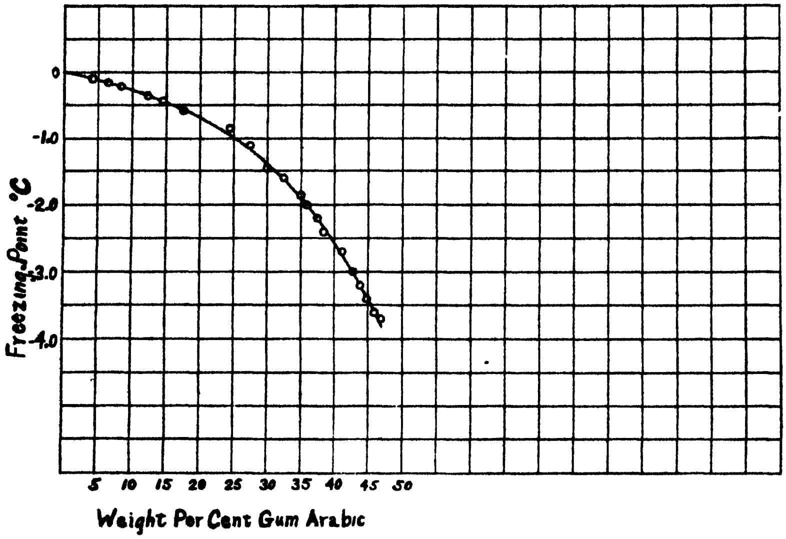

Fig. 4
Freezing Point as a function of concentration.

TABLE VII

Freezing Points of Gum Arabic Water Solutions

No.	Wt. % G.A.	F.P.	No.	Wt. % G.A.	F.P.
1	4.38	−.100	13	30.0	−1.4
2	5.83	−.136	14	32.5	−1.6
3	6.51	−.148	15	35.0	−1.8
4	7.55	−.165	16	36.0	−2.0
5	8.41	−.198	17	37.5	−2.2
6	12.45	−.356	18	38.5	−2.4
7	14.52	−.430	19	41.2	−2.7
8	15.13	−.456	20	42.8	−3.0
9	17.55	−.563	21	43.8	−3.2
10	24.5	−.85	22	44.8	−3.4
11	27.5	−1.1	23	45.9	−3.6
12	29.0	−1.2	24	46.9	−3.7

Newton and Gortner[1] have determined the freezing point of gum arabic solutions up to a weight concentration of nine per cent. Their results show freezing points somewhat higher than those here recorded. These investigators do not state the method of purification or the water content of the material used in their determination as they were interested in relative data only. We have determined the freezing point of our starting material (i.e. crude gum containing approximately 10% water) and have found results practically identical with those of Newton and Gortner. The freezing points of the crude gum were determined over the same range as that of the purified gum and were found to be considerably higher. The solution containing forty-five weight per cent of crude gum has a freezing point depression of about one-half that of the purified gum. These differences are not explainable upon differences of water content alone but point to differences in the hydration of the two samples.

Conductance Data for Gum-Arabic-Water Systems

The conductance of five concentrations of gum arabic at 30° was determined by the aid of the usual conductivity cells using a Leeds and Northup slide wire bridge. Two cells were used, one having a cell constant of 0.448 and the second of 0.103. The constants were obtained by calibration of the cells with solutions of potassium chloride, the data of the International Critical Tables for the conductances of these solutions being used as the basis of the computation. The two most dilute solutions and the conductance water were determined in the cell having the smallest cell constant. The data obtained are given in Table VIII.

TABLE VIII

The Conductances of Gum Arabic Solutions.

Conc. gms/1,000 gms H_2O	N	R (Ohms)	k	Λ_v
215.8	0.180	84	0.00534	26.69
21.58	0.0180	530	0.000847	47.10
2.158	0.0018	4760	0.0000942	52.38
0.2158	0.00018	9000	0.0000097*	53.94
0.02158	0.000018	38000	0.00000099*	55.09
Cond. Water	0	60000	0.00000172	

* Corrected for the specific conductance of water.

N represents the normality of the solution on the basis that 1200 is the equivalent weight[2] of gum arabic and Λ_v is the equivalent conductance, i.e. the specific conductance, k, times the volume in cc containing one gram equivalent.

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[1] Bot. Gaz., **74**, 442 (1922).

[2] Thomas and Murray: two values were obtained by these investigators but this value seems the more reliable one. It should be remembered that their value was for arabic acid. Here, as will be pointed out, we are probably dealing with a salt of somewhat higher equivalent weight. The uncertainty in the equivalent weight of the acid, however, does not warrant any correction for the replacement of hydrogen by calcium or magnesium.

Discussion of Results

The viscosity of a true lyophilic sol, presents the following generally recognized characteristics:

a. At constant temperature the viscosity increases more rapidly than concentration of dispersed phase. In some instances the addition of relatively small amounts of dispersed phase (a few weight per cent) will produce a viscosity many times greater than that of the dispersion medium at the same temperature.

b. The temperature coefficient of viscosity is considerably larger than that of the dispersion medium. This is especially marked for sols which set to gels in the neighborhood of their gelation temperatures. In this connection the relative viscosity usually shows a considerable decrease with rising temperature.

c. The viscosity is a function not only of concentration and temperature, but also of the history of the system under examination. Such factors as the mechanical and thermal treatment to which the system has been subjected may influence the viscosity to a marked extent. Very likely the majority of these influences may be traced to their effects upon the degree of dispersion or upon the volume of the colloidal phase.

d. The electrical charge of the particle is also a determining factor in the viscosity of these systems. A reduction of the charge upon the particle presumably has the effect of reducing its size and thereby the viscosity of the system. This phenomenon has been termed by Kruyt[1] "the electroviscous effect". The reduction of charge may be secured by the addition of electrolyte, the ion having a charge opposite to that of the colloidal particle is supposedly the effective one.

An examination of the viscosity data obtained for gum arabic shows that to some extent it resembles those of lyophilic sols. The viscosity increases more rapidly than concentration, the temperature coefficient is greater than that of water, the relative viscosity diminishes with rising temperature and the addition of calcium chloride reduces the viscosity of these systems as compared to that of the dispersion medium.

On the other hand, the viscous behavior of true solutions must be considered. In the case of quite soluble organic substances the viscosity increases more rapidly than does concentration, the behavior being most marked at high concentrations. To be specific, the viscosity data for three substances at 30°C are plotted as functions of their concentration in aqueous solution in Fig. 5. Curve I represents the data of gelatin, a true lyophilic colloid, Curve II that of gum arabic taken from Table I and Curve III that of cane sugar, a non-electrolytic solute. Values for calcium chloride solution, an electrolytic solute, up to thirty weight per cent are nearly identical with those of Curve III.[2]

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[1] "Colloids" (trans. by van Klooster), 172 (1927).

[2] The data for calcium chloride solutions is that of the International Critical Tables. Thirty per cent does not mark the limit of solubility at this temperature but is the extent of tabulated data. Without doubt the curve would show an upward trend if data were available to its saturation value of approximately fifty weight per cent.

As will be seen gum arabic occupies an intermediate position with respect to the other two substances.

The temperature coefficients of true solutions are as a rule greater than that of water and become quite large at high concentration of solute. Thus the temperature coefficient of a sixty per cent cane sugar solution between 25°C to 40°C is 4.9; that of water over the same temperature range is 2.07.[1]

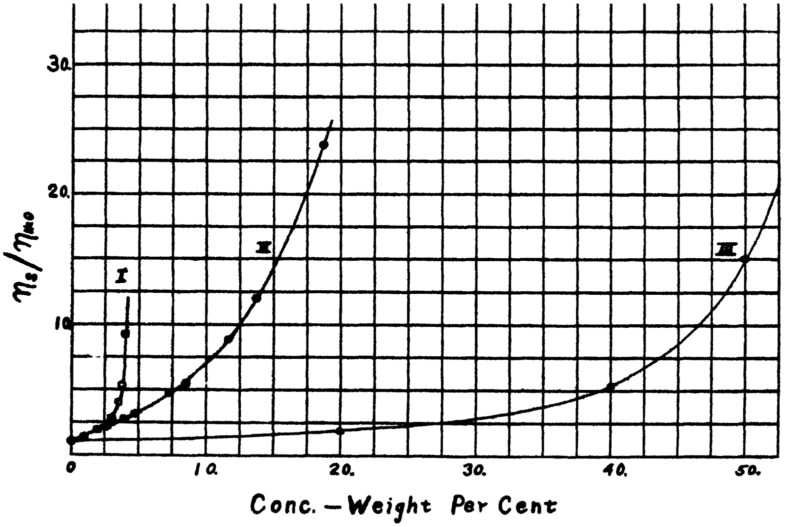

FIG. 5

Viscosity as a function of concentration.
Curve I–gelatin sols (extrapolated from data of Bogue: J. Am. Chem. Soc., 43, 1764 (1921); Curve II–gum arabic solutions (data from Table I); Curve III–Cane sugar solutions (data of Bingham and Jackson: Sci. Paper B. of Stds. 298, 1917).

That of the gum arabic solution of approximately 10 weight per cent is 2.55. If the temperature coefficient had been determined for the more concentrated solutions of gum arabic it would undoubtedly have been large. An examination of Tables II and III will show that an approximate doubling of the weight concentration produces nearly a twenty per cent increase in the tempperature coefficient in the interval 30° to 45°.

Greater attention has been paid to the changes in the relative viscosity with temperature than to the variation of the temperature coefficient, especially so since Ranken and Taylor[2] pointed out that in general the relative viscosity of electrolyte solutions increased with rising temperature, while the reverse holds true for solutions of non-electrolytes. Lyophilic sols show the same behavior as organic solutes, i.e. there is a decrease in the relative viscosity with rising temperature.

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[1] Computed from ICT data.

[2] Trans. Roy. Soc. Edin., 45, 397 (1906).

In the case of the gum arabic systems the relative viscosity decreases with rising temperature as has been shown in Fig. 2. If the gum is a mixture of the salts of arabic acid it would be both an organic solute and an electrolyte. If this view is correct the organic character of the material plays a greater part in the determination of the relative viscosity than does its electrolytic behavior. Moreover, the distinction of Ranken and Taylor given above is not an absolute one. There are a considerable number of exceptions to the rule, the most noticeable of which are certain salts of magnesium.

Still another viscosity function of some significance is one having the form $\frac{\eta_s/\eta_0 - 1}{F}$, where η_s/η_0 is the relative viscosity and F the concentration of solute in gram equvialents. Gruneisen[1] pointed out that this function had a minimum value when plotted against the concentration for solution of electrolytes, but no minimum was apparent for non-electrolytes. Since the quantity F is not determinable for hydrophilic sols, a prediction of the behavior of this function with concentration cannot be made. Gruneisen ascribes the minimum value as being due to electrolytic dissociation. The increase of the relative viscosity per gram equivalent at the smallest concentration being explained by the assumption that increasing dissociation produces an increase in viscosity. It is interesting to note that if the concentrations of Table I are recomputed to gram equivalents and Gruneisen's function is calculated for the gum arabic solutions, that a minimum does occur as is shown in Table IX.

TABLE IX

Concentration of Gum Arabic

No.	Gm. Equiv. per liter*	$\frac{\frac{\eta_s}{\eta_0} - 1}{F}$	No.	Gm. Equiv. per liter*	$\frac{\frac{\eta_s}{\eta_0} - 1}{F}$
1	0.010	64.	8	0.063	62.
2	0.018	57.	9	0.073	62.
3	0.023	57.	10	0.10	77.
4	0.032	59.	11	0.12	91.
5	0.033	58.	12	0.15	127.
6	0.040	56.	13	0.17	136.
7	0.047	55.	14	0.33	900.

* The equivalent weight assumed for gum arabic is 1200 as taken from data of Thomas and Murray. See page 883.

Although the function $(\eta_s/\eta_0 - 1)/F$ is somewhat irregular at first, it passes through a well defined minimum at a concentration of 0.047 N. This is of significance when taken into consideration with the other arguments to be developed.

In this same connection should be noted the effect of additions of calcium chloride upon the viscosity of the gum arabic solutions. The reduction to a minimum value of viscosity occurs at far larger concentrations of electrolyte than do the minimum values which Kruyt finds in the cases of true hydrophilic sols. In these cases the reduction to a minimum value occur at concentration of a few milli-equivalents of electrolytes. In the case of gum arabic, reduction to the minimum value occurs at approximately two hundred milli-equivalents, many times that of Kruyt's values. We are inclined to believe that *the reduction of viscosity here is due to repression of ionization of the calcium and magnesium arabates* and to the influence of the added electrolyte upon the hydration of the gum arabic, rather than to the reduction of the electrokinetic potential upon particles of gum arabic.

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[1] Wiss. Abh. phys.-techn. Reichsanstalt, 4, 239 (1905).

The last consideration to be made of the viscosity determination is the effect of neutral salts upon the systems under consideration. An inspection of Table V shows that while the effect of the salts differ to some extent among themselves, and the order is that in general of the lyotropic series, the effect of the iodides and thiocyanides are not as marked as is usually the case for lyotropic effects.

Kruyt[1] ascribes the lyotropic effect to two factors: (1) hydration of ions (2) disturbance of the water equilibria (i.e. those involving dihydrol, monohydrol, etc.).

If this be so, the slight variations which occur in the cases of gum arabic solutions could be ascribed to the first factor; the considerable reduction of all solutions containing electrolyte to the second. Gum arabic in the presence of water is itself without doubt heavily hydrated as judged by its high solubility and high effective density. The addition of ions would result in removal therefore of some of the solvent. If this effect were large an increase of viscosity would result due to the reduction in the mass of the solvent. Actually a decrease occurs, the decrease being approximately the same for all salts.

Density

Wintgen[2] has pointed out that the specific volume of a number of colloidal solutions is a linear function of the weight per cent of the disperse phase, the density being a linear function of the number of grams of disperse phase present in a volume of 100 cc of solution. From the density data given in Table I, it has been found that the specific volume, V, can be computed with considerable accuracy (the variations are considerably less than 1% between calculated and observed values up to 20 weight per cent) by means of the equation:

$$V = 1.004 - .00374P$$

where P represents the weight per cent of gum arabic in solution. The value of V at $P = 100\%$ is 0.627. The density of the gum computed from this specific volume is 1.59 as compared to that found directly of 1.48.[3] The effective densities given in Table I are the equivalent of this quantity and were computed by deducting the volume of water present in a given mass of solution from the volume of the solution and dividing this quantity by the mass of gum present.

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[1] "Colloids," 184 (1927).

[2] Kolloidchem. Beihefte, 7, 251 (1915).

[3] This was found by using mixtures of toluene and carbon tetrachloride and determining the density of the mixture which just floated the purified gum. The original crude gum had a density of 1.51 by this method. The determinations were made at 15°C.

Wintgen likewise found large effective densities for the systems examined by him and ascribes the large values to a film of condensed water about each particle. The fact that systems of gum arabic and water show analogous density relations to the colloidal systems investigated by Wintgen should not be taken as evidence for their colloidity. Wintgen himself points out that similar relations hold true for solutions. In the case of cane sugar an equation of the form

$$V = 1.0043 - 0.003860P$$

holds with precision at 30° up to 10 weight per cent. This concentration is approximately of the same molar concentration, as the most concentrated gum arabic solution used if its molar weight is assumed to be 2400. The extrapolated density of solid cane sugar from the above equation is 1.62 which again is higher than the density of solid cane sugar alone (1.59).

Freezing Point Determinations

The important facts to be noted about the data of Table VII and Fig. 4 are (a) the considerable magnitude of the freezing point depression and (b) the increasing magnitude of freezing point depression per unit of mass of solute as indicated by the convexity of the curve toward the concentration axis. If the molecular weight of 2400[1] for gum arabic be assumed, the molar freezing point depression over a range of concentration can be computed. About one-half of the values given in Table IV have been recomputed to a molal basis and the ratio of freezing point depression to molal concentration likewise computed. These are given in the following table, where No. refers to the observations of Table IV, F the molal concentration and ΔT the observed depression.

The striking features about the values of $\Delta T/F$ so calculated are (1) the fact that these values are of the correct order of magnitude for di-monovalent salts;[2] (2) the variations of $\Delta T/F$ with concentration are characteristic of a

TABLE X

No.	F	$\Delta T/F$	No.	F	$\Delta T/F$
1	.019	5.3	11	.16	6.9
2	.029	5.1	13	.18	7.8
5	.038	5.2	16	.23	8.7
6	.059	6.0	19	.29	9.3
7	.071	6.1	22	.34	.10
9	.089	6.3	24	.36	9.7

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[1] The titration curves of Thomas and Murray show plainly that arabic acid is a monobasic acid. Calcium arabate would therefore be Ca (Arabate)$_2$. We have used the approximate value of 2400 as the molecular weight. See also page References 883, footnote 2.

[2] For example the value of $\Delta T/F$ for magnesium chloride at 0.025 M is 5.03; compare this value with that of the gum arabic at 0.029 M.

large number of salts, i.e. it starts with a given value, decreases in value with increasing concentration to a minimum and finally increases to a much larger final value. It is true that the increase to high final values for most electrolytes takes place at much greater molal concentration than that found in this case, but it must be remembered that a molal concentration of 0.36 in this case corresponds to a weight concentration of nearly fifty per cent. The evidence from the freezing point data is therefore added proof, to our minds, of the salt-like character of gum arabic.

Conductance Data

If the equivalent conductances of the gum arabic solutions are plotted against the logarithms of their dilutions there is obtained the curve shown in Fig. 6. This is the typical curve obtained for a large number of electrolytes and when added to the evidence previously adduced leaves little doubt in our minds that gum arabic solutions are actually solutions of calcium and magnesium arabates. Further the equivalent conductance as above computed is a linear function of the square root of the concentration as is shown in Fig. 7. This extrapolated to the value of c = 0 gives the equivalent conductance of the gum at infinite dilution, the numerical value of this quantity being 55.5 mhos. At this temperature the value for the equivalent conductance at infinite dilution of the calcium ion singly is 66.1 mhos; that for magnesium ion is 58.8 mhos.[1] *The equivalent conductance of the gum is of the same order of magnitude as that of its positive ions*, i.e. the positive ions are the chief carriers of the current in these solutions. The fact that the equivalent

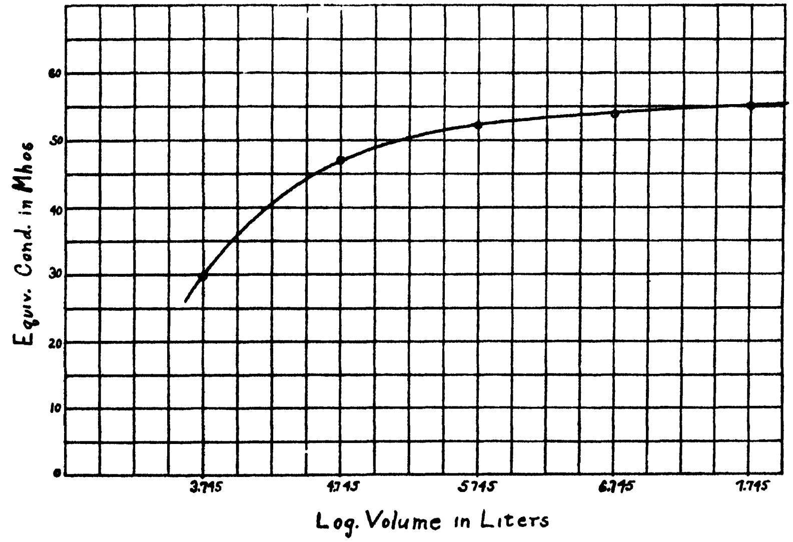

FIG. 6
The Equivalent Conductances of Gum Arabic Solutions.

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[1] ICT, 6, 230 (1929).

conductance of the salt is somewhat less than that of either of the positive ions has possible explanation in that the value found for conductances at infinite dilution will depend upon the method of extrapolation (which is different for Ca^{++} and Mg^{++}) and in the second place the conductance of the calcium (or magnesium) ion would doubtless be affected by the presence of the tremendously larger arabate ions. The fact that the equivalent conducttance of the gum is practically that of its positive ions would naturally be expected if gum arabic is a mixture of calcium and magnesum arabates. The very large and heavily hydrated anion of low charge (monovalent) could not be expected to transport any great fraction of the current.

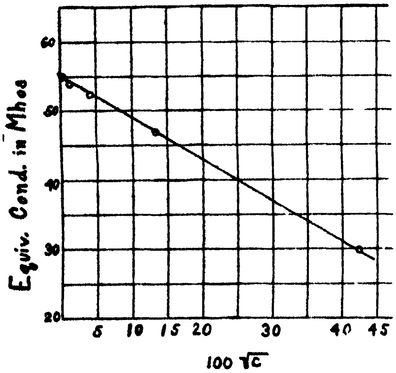

FIG. 7

The Equivalent Conductance as a function of the Square Root of the Concentration (actually 100 $\sqrt{c}$)

Again it should be noted that the data obtained for gum arabic solutions is not explainable upon the basis of McBain's theory of colloidal electrolytes,[1] for in this case the osmotic activity is the same as that of di-monovalent salt, but the equivalent conductance is about one-half that of many electrolytes. Further there is no evidence of the formation of ionic micellae with increasing concentration as the value of $\Delta T/F$ for the gum arabic solutions increases at higher concentrations of the gum and at no time is less than that corresponding to salts of the type MX_2. The contrary is true for soap solutions upon which McBain's theory is based. It should also be pointed out that the lack of gel formation in the case of gum arabic solution is considerable evidence that the aggregation tendency of this material is not great. We have kept systems containing over fifty per cent by weight of gum arabic at zero degrees or lower for many hours with absolutely no evidence of gel formation, the system remaining as a highly viscous one, which upon further cooling separated solid solvent.

pH Measurements

Thomas and Murray (l. c.) have called attention to the fact that arabic acid is a strong monobasic acid as evidenced by the sharpness of the single break of its titration curve. The pH measurements which we have made would tend to confirm this conclusion. The pH of these solutions (determined at 25°) are only slightly greater than that of neutrality and vary but little with concentration (Table I). The presence of neutral salts increases these pH values slightly (Table V).

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[1] Bogue: "Colloidal Behavior," 1, 410 (1924).

Conclusion

From the physico-chemical data here found and those furnished by Thomas and Murray, it would appear that the majority of properties of gum arabic solutions can best be interpreted on the basis of the so-called classical theory of solutions.

The protective action of gum arabic solutions which has been known for many years[1] could be explained as due to the high viscosity of these solutions and to the probable high adsorption of the gum arabic molecules. It is well known that many organic molecules show a high adsorbability. The high viscosity, preventing rapid attainment of hydration equilibrium, could also be used to account for the variability of certain properties with time or method of preparation.[2] In the next place certain properties such as the osmotic pressure of gum arabic solutions will be modified by the presence of a large non-diffusible ion. The application of the Donnan theory of membrane equilibria has been successfully applied by Thomas and Murray to such cases.[3]

Still further evidence for our views is found in the lack of solubility of gum arabic in organic solvents as we have previously pointed out.[4] Gum arabic will not dissolve appreciably in any other common solvent than water with the possible exception of ethylene glycol and glycerol. Walden[5] has pointed out that a given electrolyte will show the greatest solubility in a solvent of high dissociating power (i.e. high dielectric constant). The problem is complicated in the case of this solute by the undoubted fact that considerable solvation must accompany solution. The combined ability of water to both solvate and ionize this substance may account for its high solubility in this medium.

Lastly, water solutions of our purified gum arabic give the precipitation reactions of calcium and magnesium salts. If ammonium oxalate is added to a gum arabic solution a precipitate is formed immediately. If this precipitate is filtered off, and the filtrate made alkaline with ammonium hydroxide, a precipitate can be produced by the addition of sodium phosphate. These are the qualitative reactions of calcium and magnesium salts. It should be remarked that the precipitation of calcium oxalate is considerably more abundant from a given mass of gum arabic than is that of magnesium ammonium phosphate. Solutions of our material gave no precipitate in solutions made alkaline with ammonium hydroxide when saturated with hydrogen sulfide, indicating the absence of any heavy metal.

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[1] Lefort and Thibault: J. Chem. Soc., **42**, 1322 (1882).

[2] The most noticeable case of such variation is found in the double refraction of gum arabic solutions. Hill (Phil. Mag., **48**, 487 (1899)) in measuring double refraction states that the value obtained depends upon the mode of preparation.

[3] We are not in complete accord with these authors, however, upon the application of the Donnan theory to the viscosity effects which result upon the addition of electrolytes. From the results which we have obtained it would appear as if we were dealing with arabate ions and not arabate micellae as Thomas and Murray have assumed. The maximum value of viscosity obtained by these investigators at pH 6.2 is difficult to explain but it must be remembered that similar phenomena occur in other true solutions. Thus the addition o sulfuric acid to nitric acid produces a mixture of lower viscosity than the original nitric acid (Bingham and Stone: J. Phys. Chem., **27**, 701 (1923)). Such variations are ascribed to changes in solvation and ionization.

[4] Tran. Kansas Acad. Science, **32**, 49 (1929).

[5] Z. physik. Chem., **61**, 633 (1908).

Summary

1. The viscosities, densities, pH values, freezing points, and conductances of gum arabic-water systems have been determined over a considerable range of concentrations. Some viscosity and density measurements have been made through a range of temperatures.

2. These properties are most easily explained by assuming that purified gum arabic is a strong organic electrolyte of high equivalent weight, rather than existing as a colloidal phase when in contact with water.

University of Kansas,
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THE RÔLE OF HYDROCYANIC ACID VAPORS IN THE CORROSION OF IRON

BY J. F. G. HICKS

During the course of the writer's investigation as to the cause of the corrosion of iron, his attention was directed to the disastrous effects of hydrocyanic acid vapors in connection with the internal corrosion of gas-mains. This substance always present in municipal gas, brings about the gradual conversion of metallic iron to dark-blue substances closely approximating the composition of Prussian Blue,[1] which, in the form of dust, ultimately brings about stoppage of service at many points.[2] At this time the question arose as to whether this type of corrosion offered anything new in principle, or whether it merely represented another phase of the general process of corrosion of metals above hydrogen in the electromotive series.[3]

Those investigators who have most carefully studied the principles underlying the process of the corrosion of iron, are, without exception, men not connected with the gas-industry, and they are uniformly silent as to the function of hydrocyanic acid in that process. So far as a study of the literature revealed, this acid is present in all manufactured gas, and the majority of internal-corrosion-products contain the blue substance closely akin to "Prussian blue"; indeed the samples examined contained as high as 91.27% of it.[4] For this reason it is highly important to determine the function of hydrocyanic acid in the process of the corrosion of iron: in other words, is it contributory or causatory?

There is quite a diversity of opinion among the contributors to the literature of gas-technology as to the actual cause of internal corrosion of gas-mains, O_2, CO_2, a mixture of these two (in the presence of moisture) and HCN all being assigned causatory and contributory parts. As the writer views it,[5] this diversity of opinion is due chiefly to the fact that these investigators have failed to distinguish between a causative agent and an accelerator, much as did Howe.[6] Thus, Taplay and Parkinson[7] consider HCN as the *primary corrosion-agent, and note the accelerating-effect of O_2*, while

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[1] See footnote to Table I, this article.

[2] The internal corrosion-rate of Portland City gas-mains has been estimated at about an average of 0.001 lb./ft.2/yr., a yearly total of 9500 lbs. Fe = 10 tons Prussian blue.

[3] J. Phys. Chem., **33**, 789, 790 (1929).

[4] See this article, Table I.

[5] J. Phys. Chem., **33**, 780 (1929).

[6] Howe: Am. Soc. Test. Mat., **8**, 278T (1908).

[7] Taplay and Parkinson: Chem. Abs., **13**, 1919; Gas J., **146**, 622; Gas World, **70**, 451 (1919).

Taplay later[1] asserts that "corrosion may be brought about in at least six different ways", citing as the six causatory agents HCN, CO_2 excess O_2, CO, SO_2, and "the products of the reaction between NH_3 and CS_2" (most probably thiocyanates). Coleman[2] definitely states that "HCN initiates corrosion, which is carried on by the normal rusting action of moist carbon dioxide and oxygen"; the occurrence of Prussian blue in the observed frequency and relative quantity, however, would not tend to support this view.[3] Richardson[4] and Williams[5] consider that the action of HCN in the corrosion-process is subsidiary, and that moist O_2 and CO_2 *together* initiate corrosion, and conclude that corrosion need not necessarily cease if HCN be eliminated.

TABLE I

Iron Compounds found in Corrosion-Deposits (in per cent), Dry Basis

Sample No.	1	2	3	4	Averages
Ferric Oxide	2.75	0.87	3.75	4.63	3.00
Ferric Sulfate	0.87	0.62	1.95	2.01	1.36
Ferrous Sulfide	1.12	1.39	0.00	1.95	1.12
Prussian Blue[6]	74.19	85.12	91.27	89.56	85.04
Totals	78.93	88.10	96.97	98.15	90.52

Upon conversion to metallic iron the above data yields:

Sample No.	1	2	3	4	Average	Factor to multiply above percentages
Ferric Oxide	1.93	0.61	2.63	3.24	2.10	$\frac{2Fe}{Fe_2O_3} = 0.70$
Ferric Sulfate	0.35	0.22	0.78	0.80	0.54	$\frac{2Fe}{Fe_2(SO_4)_3} = 0.40$
Ferrous Sulfide	0.72	0.91	0.00	1.15	0.72	$\frac{Fe}{FeS} = 0.64$
Prussian Blue	34.13	39.16	41.98	41.20	39.12	$\frac{7Fe}{Fe_4[Fe(CN)_6]_3} = 0.46$
Totals	37.13	40.90	45.39	47.39	42.48	
% total iron as Prussian Blue	91.92	95.75	92.50	86.94	91.78	$\frac{\%Fe \text{ as Prussian blue}}{\text{Sum of } \%Fe \text{ in each component.}}$

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[1] Taplay: Chem. Abs., **14**, 2411; Gas J., **150**, 583; Gas World, **72**, 481 (1921).

[2] Coleman: Gas J., **162**, 794 (1923).

[3] This article, Tables I, II, and comments.

[4] Richardson: Chem. Abs., **17**, 2493 (1923); **18**, 580 (1924); Gas J., **162**, 348 (1921); **164**, 515 (1923); Gas World, **79**, 468 (1924).

[5] Williams: Chem. Abs., **17**, 2493, 2749; Gas J., **162**, 725 (1923).

[6] When the blue iron-compounds are analyzed, (CN) is determined and calculated to Prussian blue by means of the factor $\frac{Fe_4[Fe(CN)_6]_3}{18\ (CN)} - 1.795$. In reality, however, no analyses made during the course of this investigation ever indicated a compound exactly corresponding to that of Prussian blue: they yielded 53.75 – 54.28% $(CN)^-$. The theoretical value for Prussian blue is 54.42% $(CN)^-$. A sample from Merck (Blue Label) yielded 54.20%, and one prepared in the laboratory 54.10% $(CN)^-$.

Bertelsmann[1] assumes a rather non-committal attitude, holding that moist O_2, CO_2 and sulfur-compounds are the causes of internal corrosion, and at the same time admitting that HCN is highly destructive as a corrosive agent.

Some idea as to the importance of HCN in the process of internal corrosion may be had from Table I.

The fact that the corrosion-deposits averaged a percentage of iron equal to 42.70% of the dry sample, of which iron an average of 91.78% was found to be in the form of Prussian Blue, renders the determination of the function of HCN in the internal corrosion process highly important.

Possible Corrosion Products; Their Susceptibility to Attack by HCN.

Consideration of Table I would suggest that Prussian blue is the final product of internal corrosion, and it therefore follows that there should be some intermediate products. The nature of these will depend upon the composition and relative concentration of the several corroding-agents present. These are as follows:

TABLE II

Corroding Agents

Corroding agent	Present in % by volume	Action in the Corrosion Process
CO	6.80	Forms carbonyls of iron which remove iron by volatilization and mechanical transfer.
CO_2	0.95	Forms H_2CO_3 (with water vapor)[2] and hence increases concentration of H^+.
O_2	0.10	Depolarizes[3]; forms $Fe(OH)_3$, less soluble than $Fe(OH)_2$.
CS_2	0.02	Form HNCS (strong acid) and H_2S[4].
NH_3	0.001	
HCN	0.004	Forms blue compounds like Prussian blue, and thereby removes $Fe(OH)_2$ and $Fe(OH)_3$.

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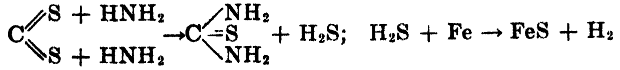
[1] Het Gas, **42**, 142 (1922); Gas und Wasserfach, **65**, 43, 686 (1922).

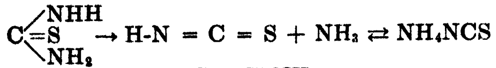
[2] J. Phys. Chem., **33**, 784 (1929).

[3] J. Phys. Chem., **33**, 783-4 (1929).

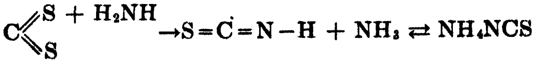
[4] Perhaps this can be best explained by the following system of equations:

(1) 

$$C\begin{cases}S + HNH_2\\ S + HNH_2\end{cases} \rightarrow C\begin{cases}NH_2\\ =S\\ NH_2\end{cases} + H_2S;\quad H_2S + Fe \rightarrow FeS + H_2$$

(2) 

$$C\begin{cases}NHH\\ =S\\ NH_2\end{cases} \rightarrow H\text{-}N = C = S + NH_3 \rightleftarrows NH_4NCS$$

(3) Or, possibly: 

$$C\begin{cases}S + H_2NH\\ S\end{cases} \rightarrow S=\dot{C}=N-H + NH_3 \rightleftarrows NH_4NCS$$

It will be noted that most of the corroding-agents are present in relatively small quantity; the highest volume-percentage, and in fact, the only one above 1%, that of CO, is scarcely sufficient to be considered in the light of a serious corrosion-factor. Yet previous work has shown the high degree of activity of both CO_2[1] and O_2[2] in this respect, and the magnitude of the effect of HCN (next to the lowest concentration of any corroding-agent) has already been referred to (introduction). Altho no H_2S is permitted to escape into the mains, some FeS has been observed, due to the formation of H_2S in the mains.[3] The presence of moist CO_2 (= H_2CO_3) would naturally suggest the "intermediate" $Fe(HCO_3)_2$, rapidly changing to $FeCO_3$. As no carbonate has been found in any corrosion-product in situ, these two substances would be relatively low persistency if formed at all (see Table III). We have therefore, logical ground to consider the following "intermediates" in the process of internal corrosion:

1. Ferrous carbonate
2. Ferrous sulfide
3. Ferrous hydroxide (hydrated, xH_2O).
4. Ferrous ferrite, (hydrated Fe_3O_4), Fe $(Fe_2O_4).xH_2O$ (intermediate between Fe^{++} and Fe^{+++}).
5. Ferric hydroxide (hydrated, xH_2O).
6. Ferric oxide (hydrated, xH_2O) ("rust").
7. Ferric sulfate, basic, $xFe_2(SO_4)_3.yFe(OH)_3$.

The behavior of these "intermediates" with respect to HCN was then studied in detail. All tests were made in sealed Erlenmeyer flasks, filled to the stopper with 0.075 (approximately 2%) HCN solution; all dissolving, precipitating and washing were performed in closed vessels, using boiled distilled water, as per Fig. 1. Should any of these "intermediates" be acted upon by HCN they should be rightly considered as such; if not, as "final" corrosion-products. As has been previously pointed out, the marked excess of Prussian blue very strongly suggests it as a final product of internal corrosion.

Samples to be directly tested were weighed out; precipitated material was prepared from aliquots of standardized stock solutions using such quantities that as nearly as possible the same weight of "from stock" and "freshly precipitated" materials was submitted to the test. The samples were treated with a quantity of 0.075 N.HCN solution containing twice the quantity of HCN necessary to convert each to ferrocyanide, and the whole allowed to stand for 100 days, after which it was analyzed for CN-content. The %(CN^-) in the residues was taken as a measure of their susceptibility to HCN-action and also as a rough measure of the rate of this action. The value of a test of this character is comparative rather than specific. It is not so much a question of *how much* of a given substance will be altered by HCN solution or *how rapidly* it will be altered, as it is a question of the *order of susceptibility* to HCN-action. The results of these tests simply indicate the course of transition from intermediate to final products and the comparative rate of transition.

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[1] J. Phys. Chem., 33, 784 (1929).

[2] J. Phys. Chem., 33, 783-4 (1929).

[3] $H_2S + Fe \rightarrow FeS + H_2\uparrow$. See equation (1) footnote preceding page.

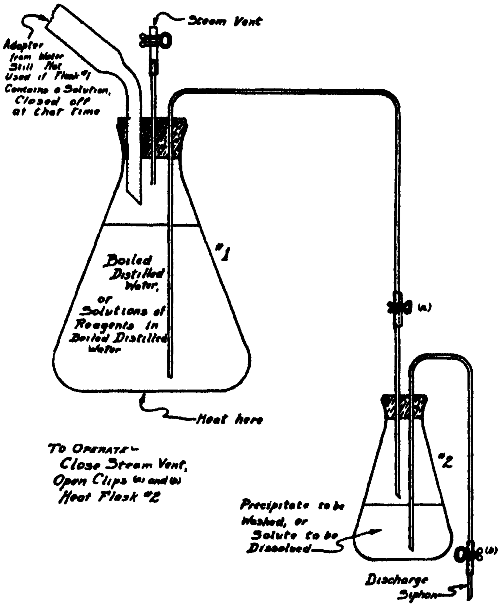
Adapter from Water Still Not Used if Flask #1 Contains a Solution, Closed off at that time
Steam Vent
Boiled Distilled Water, or Solutions of Reagents in Boiled Distilled Water
#1
(a)
Heat here
To Operate—
Close Steam Vent,
Open Clips (a) and (b)
Heat Flask #2
#2
Precipitate to be Washed, or Solute to be Dissolved
(b)
Discharge Siphon

FIG. 1

Due to differences in degree of aggregation, there will be wide differences in physical characteristics (and therefore in susceptibility to solvent or the chemical action at the surface) between a freshly-precipitated substance, and the same substance after having stood for some time or "as purchased". This is due to gradual transition from colloidal to crystalline state, to change in degree of hydration, or both. In a series of tests like these under discussion, it would be essential that a freshly precipitated substance be washed free of dissolved electrolyte, and it would therefore be both colloidal and highly hydrated, all of which means that it would tend to approach maximum particle-surface and therefore maximum susceptibility to solvent or the chemical action at the surface. Crystalline substances would represent the other extreme; any number of intermediate conditions would be possible. Results are summarized on Table III:

TABLE III

Relative Susceptibility to HCN-action of the possible "intermediates" in the internal corrosion-process: 100-day test

No.	Substance tested	Physical Characteristics	% (CN) by wgt. in product, after 100 days	Remarks
1.	Ferrous Carbonate hydrated, precipitated.	Colloidal; washed free of ions other than Fe^{++} and $(CO_3)^{=}$	1.21	Maximum surface, due to highly hydrated colloid particles.
2.	Ferrous Carbonate, anhydrous, J. T. Baker's "C.P."	Microcrystalline.	0.00	Too dense; minimized surface for reaction in small crystals. Requires presence of H_2CO_3 or O_2 before HCN attacks; compare (5).
3.	Ferrous Sulfide, hydrated, precipitated.	Same as (1).	10.52	Same as (1). Seems to be more susceptible to HCN than any of the materials tested. Completion prevented because of closed container, which prevents escape of liberated H_2S.
4.	Ferrous Sulfide, anhydrous, synthetic; P.W.R. Co's. fused sticks.	Perfectly crystalline.	0.31	Readily attacked tho much less so than (3) because of the lessened surface, due to crystals; compare (3).
5.	Ferrous hydroxide, hydrated precipitated.	Same as (1)	0.00	Requires presence of H_2CO_3 or O_2 before HCN attacks. Compare (2).
6.	Ferrous ferrite ("forge-scale") fresh from forge.	Metallic iron coated with "magnetic oxide" (Fe_3O_4).	0.32	Metal and attached scale polar with respect to each other. Iron stained blue.

TABLE III (Continued)

Relative Susceptibility to HCN-action of the possible "intermediates" in the internal corrosion-process: 100-day test

No.	Substance tested	Physical Characteristics	% (CN) by wgt. in product, after 100 days	Remarks
7.	Ferrous ferrite, "Magnetic Oxide", J.T. Baker's "C.P."	Same as (4).	0.00	Same as (2) and (5).
8.	Rusted scrap-iron; "rust" means hydrated ferric oxide	Rust adhering to metal. Red, apparently lost some water.	1.53	Same as (6).[a]
9.	Ferric hydroxide, hydrated, precipitated	Same as (1).	1.33	Same as (1).
10.	Ferric Oxide, hydrated.	Same kind of "rust" as (8), *shaken, not scraped* from rusted metal.	0.92	Same as (6). Absence of metal lessens susceptibility to HCN, because no E.M.F. is possible.[a]
11.	Ferric Oxide, anhydrous J. T. Baker's "C.P."	Crypto- to micro-crystalline.	0.00	Same as (2). Compare (6) and (10).
12.	Ferric Sulfate, basic prepared in laboratory.	Colloidal, washed as in (1).	0.86	$2Fe(OH)_3.xH_2O$ (washed, colloidal) dissolved in solution of $Fe_2(SO_4)_3$, evaporated to dryness, ignited and washed until suspended.

Conclusions: (1) Prussian blue and hydrated ferric oxide are the end-products of the internal corrosion process.
(2) Ferrous compounds would be oxidized to ferric and then changed to Prussian blue.
(3) HCN cannot be a causatory agent, but only contributory.

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[a] **Aston**: Trans. Am. Electrochem. Soc., **29**, 449 (1916).

The accelerating effect of O_2 and CO_2 upon HCN-attack upon Fe:

In a previous article[1] the writer has shown that the presence of moist O_2 and CO_2 materially increased the velocity of corrosion of iron; it would therefore seem logical to determine whether the same accelerative effect was noticeable in the system Fe(metal)-HCN(vapor).

The apparatus used was the same as that used for the previous investigation (See Fig. 2) with the exception of the HCN-bottles, shown in detail in Fig. 2b. Test-pieces consisted of spirals of Malin's No. 10 gauge "music wire", and the duration of the test was fifteen days, as in the case of the similar series of tests[1] where HCN was not used. Interdiffusion of gases was prevented by keeping the gases flowing constantly in the same direction; this was accomplished by the actual pressure of the gases issuing from the containers, and by attaching a suction-pump to the other end of the system. The mercury bubbling-bottle (Fig. 2a) served the purpose of estimating and regulating gas-flow rates by bubble-counting; the HCN (Fig. 2b) bottles insured continuous entrainment of HCN-vapors by the streams of moving gases, which aspirated these vapors into the system as fast as they arose

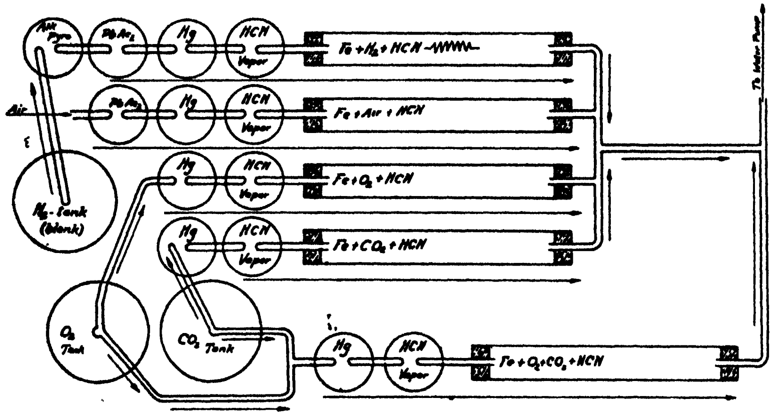

FIG. 2

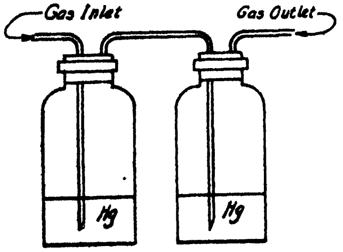

FIG. 2a

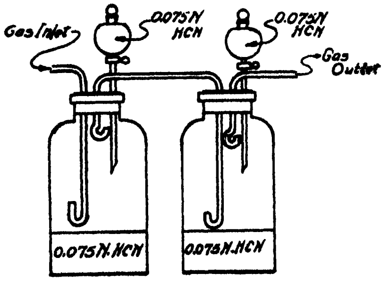

FIG. 2b

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[1] J. Phys. Chem., 33, 780 (1929).

from the surface of the 0.075 N. HCN solution. Results are summarized in the graphs below. The graphs from the previous investigation[1] are included for the sake of comparison, as they show the effect of the same corrosive agents in the absence of HCN:

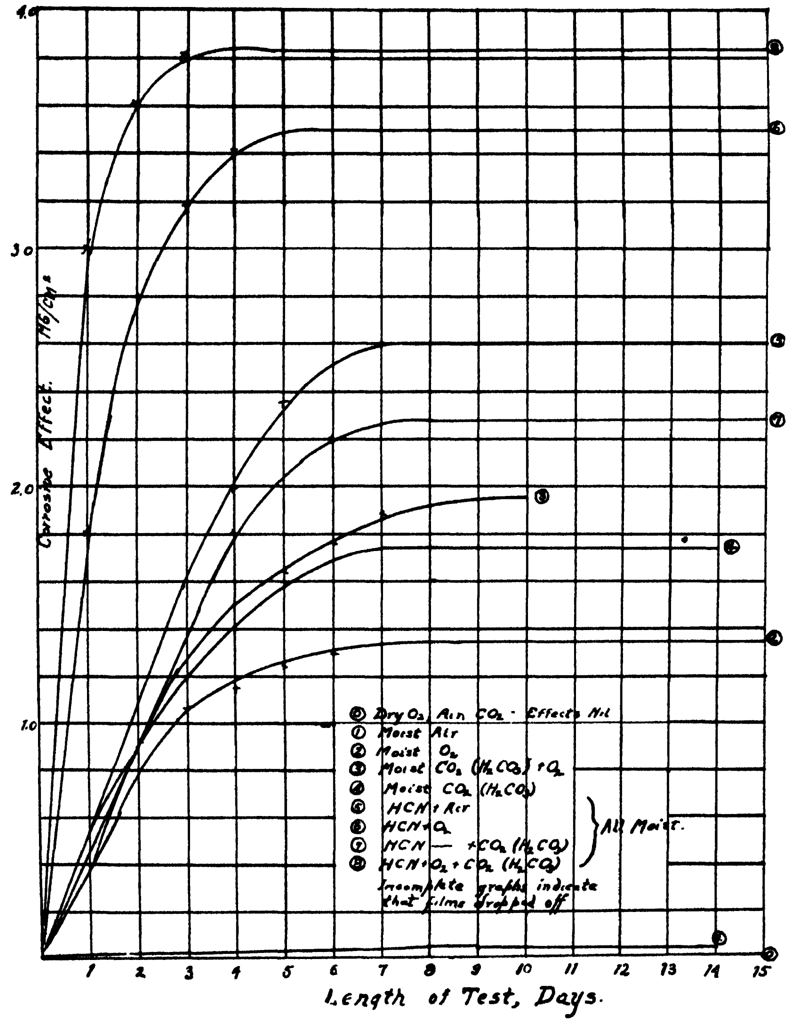

FIG. 3a

Inspection of these graphs will lead to the following conclusions:

1. HCN is the chief contributory factor in the internal corrosion of gas-mains, it being present in all cases whose graphs show high rates of corrosion and high maximum effect. H_2CO_3 and O_2 follow in order.

2. The order of intensity of effect is the order of magnitude of maxima of the graphs.

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[1] J. Phys. Chem., 33, 785 (1929).

3. The order of priority of attack is the order of priority of maxima.

4. HCN is not a cause in itself, and is subject to the same accelerative effect as other contributory factors.

Electrochemical Measurements:

The conclusions drawn from the above graphs (i.e., those concerned with HCN) were checked electrochemically, as were those from the other graphs of the previous investigation,[1] and by the same apparatus (See Fig. 4). The cells are essentially the same as those of Evans[2] but adapted to exclusion of air and the bubbling of a gas thru the electrolyte (0.075N.HCN). All electrodes were cut from the same piece of iron; in fact they were those used in the previous investigation. Eight cells, with a total of 370 sq. cm. electrode-area, were used in series for the E.M.F. readings. The cells were allowed to stand until the millivoltmeter registered equilibrium at 25°, after which the gases used were bubbled thru at the rate of 5 cc per minute until equilibrium at 25° was again recorded. The difference between equilibrium-readings (at 25°), one before and during the passage of a given gas thru the cell, represents the E.M.F. developed Results are shown in Table IV(a), which includes parallel results from the previous investigation (b) and the absolute potential difference for the same accelerator due to the presence of HCN (c).

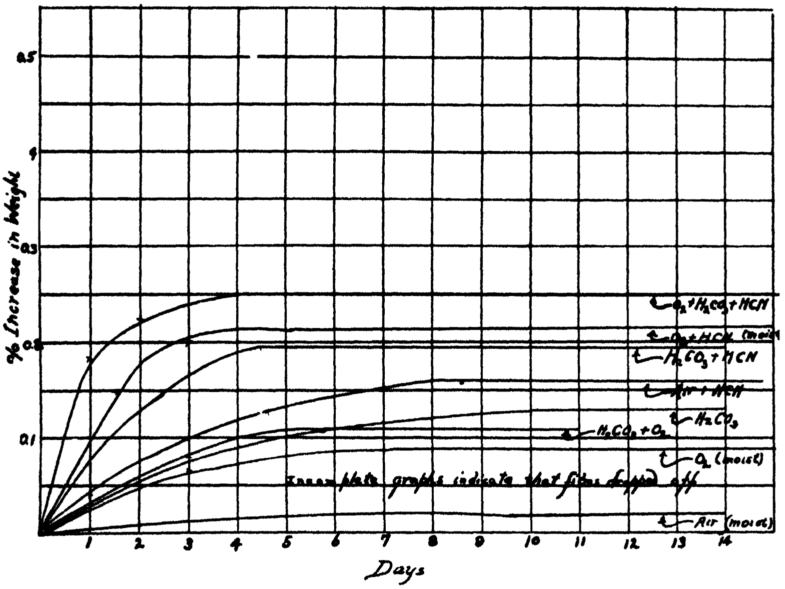

FIG. 3b

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[1] U. R. Evans: "The Corrosion of Metals," 88 (1925). Also Ind. Eng. Chem., 17, 4, 363 (1925).

[2] J. Phys. Chem., 33, 780 (1929).

TABLE IV

E.M.F. Measurements during Corrosion in the presence of HCN

No.	Gas passed thru cells	(a) Electrolyte $-0.075N$. HCN, millivolts:	(b) Electrolyte $-0.01N$ K_2SO_4, millivolts:	(c) Absolute P.D. due to HCN millivolts:
1.	air	-1.95	0.75	2.70
2.	O_2	-6.20	4.00	10.20
3.	CO_2	-2.65	0.85	3.50
4.	O_2 CO_2, (equal volumes)	-5.00	2.15	7.15

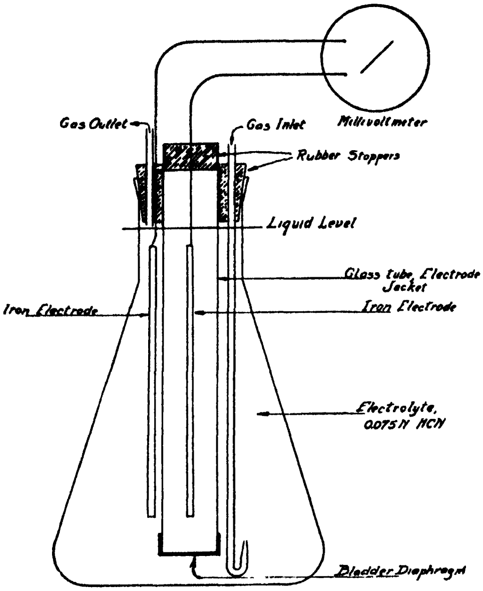

FIG. 4

Eight Cells in Series for E.M.F. readings.

When HCN is one of the concomitants of the corrosion-process, the polarity of the E.M.F. produced is negative with respect to that produced by the same accelerator in the absence of HCN. This is to be expected, since, in the presence of HCN, $Fe^{\circ} \longrightarrow [Fe(CN)_6]^{\equiv}$, while in the absence of HCN, $Fe^{\circ} \longrightarrow Fe^{++} \longrightarrow Fe^{+++}$. The profound effect of HCN is demonstrated by calculating the absolute potential difference for the same accelerator when HCN is present and when it is absent. We are therefore justified in considering HCN as the accelerator of maximum effect in the process of internal corrosion, though not a cause in itself.

Mechanism of the Process of Internal Corrosion in the presence of HCN:

It is thought that this is best represented by the following system of equations:

(1) $Fe + 2\,HOH \rightarrow Fe(OH)_2 + H_2$

(2) $Fe(OH)_2 + 2HCN \rightarrow Fe(CN)_2 + 2H_2O$

(3) $Fe(CN)_2 + 4HCN \rightarrow H_4[Fe(CN)_6]$.

(4) $2Fe(OH)_2 + H_4[Fe(CN)_6] \rightarrow \underset{\text{ferrous ferrocyanide}}{Fe_2Fe[(CN)_6]} + 4H_2O$

(5) $6Fe_2[Fe(CN)_6] + 3O_2 + 6H_2O \rightarrow \underset{\text{Prussian blue.}}{2Fe_4[Fe(CN)_6]_3} + 4Fe(OH)_3$

(6) $4Fe(OH)_3 + 3H_4[Fe(CN)_6] \rightarrow \underset{\text{Prussian blue.}}{Fe_4[Fe(CN)_6]_3} + 12H_2O$

In short, HCN (later aided by O_2) removes $Fe(OH)_2$ from the field of action and displaces the equilibrium[1] shown in (1) to the right, exactly the same as in the cases studied in the previous investigation. Hence the actual process of "cyanide corrosion" is not different in mechanism from the corrosion-process of any other metal above hydrogen in the electromotive series, i.e., HCN is a contributory or maintainence factor.

Summary and Conclusions:

1. The final product of the corrosion of iron in the interior of gas-mains is Prussian blue.

2. HCN produces the corrosive effect of maximum intensity and is first in order of priority of attack.

3. HCN is the most active corrosive agent with respect to moist iron so far studied, but is not a cause of corrosion itself; this cause is the actual dissolving of metallic iron in water, as previously concluded.[2]

4. "Cyanide corrosion" of iron differs from other processes of corrosion of iron with respect to concomitants and end-products only, but not with respect to mechanism.

5. It has been shown that HCN cannot initiate the corrosion process in the cases studied.

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[1] Professor Ulick R. Evans has been kind enough to point out to the writer that, in the 1926 edition of his "Corrosion of Metals," 157 (including footnote 2), there is to be found a similar idea as to the mechanism of the iron-corrosion-process, viz., that, when covered with a *limited* film of moisture, iron will corrode *until* this moisture film is saturated with ferrous hydroxide. In preparing his previous paper, the writer did not have access to this 1926 edition, but only to that of 1924, in which the above statement did not appear. Due acknowledgment is hereby made to Professor Evans for his appropriate and timely suggestion.

[2] J. Phys. Chem., 33, 790 (1929).

THE HEAT OF ADSORPTION OF CERTAIN ORGANIC VAPORS BY CHARCOAL AT 25° AND 50°

J. N. PEARCE AND G. H. REED

Although the thermal effect accompanying the adsorption of gases by charcoal was first noted by Mitscherlich[1] in 1843, it was not until 1874 that Favre[2] first attempted to determine the effect quantitatively by means of a mercury calorimeter. Of the numerous investigations which have been made since that time we shall cite only the more recent. Lamb and Coolidge[3] have measured the heats of adsorption of eleven organic vapors on charcoal. Keyes and Marshall[4] determined the heats of adsorption of oxygen, chlorine, carbon dioxide, ammonia and ether on gas-mask charcoal. Gregg[5] has made similar measurements for eight gases on birchwood charcoal. The ice calorimeter was used in all of these investigations. Gregg also made a few measurements with a phenol calorimeter at 40.35°. Using a potentiometric method Pearce and McKinley[6] have measured the heats of adsorption of nine organic vapors on an acid-washed, ash-free, steam-activated coconut charcoal at 25°. A comprehensive study of the heat of adsorption of oxygen on coals and charcoals at temperatures ranging from 18° to 450° has been made by a number of English investigators.[7] Their data indicate that the heat of adsorption of oxygen increases with rise in temperature. Owing to the ease of combination of oxygen with the adsorbent, and the accompanying heat effect, their results do not suffice for the calculation of the temperature coefficients of the heat of adsorption.

The heat of adsorption of hydrogen on copper catalysts, poisoned and unpoisoned, was determined by Kistiakowski, Flosdorf and Taylor.[8] Patrick and Greider[9] measured the heats of adsorption of ammonia and sulfur dioxide on silica gel. Beebe and Taylor[10] made similar measurements for hydrogen on nickel and copper catalysts, and Beebe[11] has determined the heat effect accompanying the adsorption of carbon monoxide by copper. In all of the experiments with metallic catalysts the catalyst tube itself served as the calorimeter.

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[1] Mitscherlich: Ann. Chim. Phys., (3) **7**, 15 (1843).

[2] Favre: Ann. Chim. Phys., (5) **1**, 209 (1874).

[3] Lamb and Coolidge: J. Am. Chem. Soc., **42**, 1146 (1920).

[4] Keyes and Marshall: J. Am. Chem. Soc., **49**, 156 (1927).

[5] Gregg: J. Chem. Soc., **130**, 1494 (1927).

[6] Pearce and McKinley: J. Phys. Chem., **32**, 360 (1928).

[7] Ward and Rideal: J. Chem. Soc., **130**, 3117 (1927); Blench and Garner: **125**, 1288 (1924); Garner and McKie: **130**, 3451 (1927); McKie: **131**, 2870 (1928).

[8] Kistiakowski, Flosdorf and Taylor: J. Am. Chem. Soc., **49**, 2200 (1925).

[9] Patrick and Greider: J. Phys. Chem., **29**, 1031 (1925).

[10] Beebe and Taylor: J. Am. Chem. Soc., **26**, 43 (1924).

[11] Beebe: J. Phys. Chem., **30**, 1538 (1926).

In many of the previous investigations heats of adsorption have been measured at the temperature of melting ice. Since most vapors may exist as liquids at 0°, the measured heat effect may consist of at least two heat effects, a heat of adsorption and a heat of condensation. The object of the present work was to study the effect of temperature upon the heat of adsorption. To this end we have worked at 25° and 50°, temperatures which are near, or above, the boiling points of the vapors employed. In this way it is possible to eliminate to a considerable extent at least the heat of condensation. The procedure makes possible also the calculation of the temperature coefficient of the heat of adsorption.

The apparatus used is shown in Fig. 1. It consists entirely of Pyrex tubing and flasks with no stopcocks or rubber tubing above the mercury levels. A detailed description of the apparatus is omitted since it is essentially the same as that first used by Coolidge,[12] and later by Pearce and McKinley.[6] The entire apparatus is inclosed in a large, double-walled air-bath provided with adequate means for the rapid circulation of the air. The temperature of the bath is electrically controlled by means of a four-foot mercury thermoregulator and a Bunnell relay to within ±0.05°. The adsorption bulb, shown in Fig. 2, is made of "702P" glass into which is sealed a spiral of tungsten wire. The spiral is so arranged that the ends protrude through the bottom of the bulb, thus facilitating the conduction of heat from the charcoal to the calorimeter liquid. When filled the charcoal is at no point more than three millimeters from the wire.

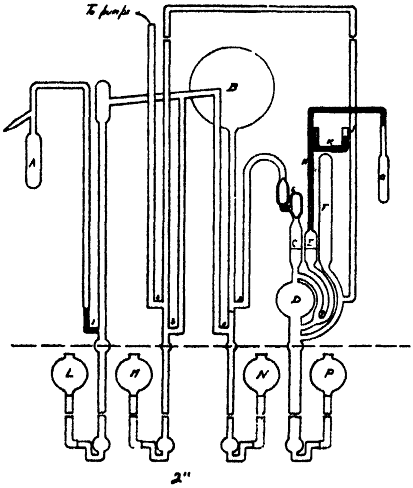

FIG. 1

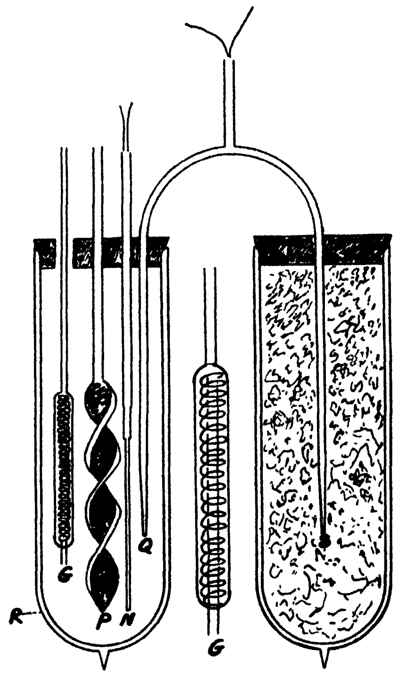

FIG. 2

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[12] Coolidge: J. Am. Chem. Soc., 46, 596 (1924).

A diagram of the calorimeter and fixtures is also shown in Fig. 2. The calorimeter is a Dewar flask fitted to accommodate the adsorption bulb, the stirrer and the heater. The water equivalent of the calorimeter and fixtures was accurately determined according to the method described by Pearce and McKinley.[6] A 24-junction copper-constantan thermocouple, made according to the specifications of White,[13] was used in conjunction with a Leeds and Northrup, Type K, potentiometer to measure the heat effects. The thermocouple was previously standardized by Dr. McKinley at the temperatures of liquid air, melting ice and the transition points of $Na_2SO_4.10H_2O$ and $MnCl_2 \cdot 2H_2O$. The thermal capacity of the calorimeter and fixtures when in use amounts to approximately 170 cals.; the thermocouple is sensitive to 0.001°. Hence, our calorimeter system will respond to a heat transfer of 0.17 cal. The calorimeter liquid is "Finol," a light oil whose specific heats at 25° and 50° were found to be 0.4528 and 0.4674, respectively.

The charcoal used as the adsorbent was taken from a large supply obtained from the National Carbon and Carbide Corporation for an exhaustive study of the adsorption of gases and vapors carried on in this laboratory. It is a coconut charcoal, steam-activated and acid-washed until the ash content is reduced to 0.28 percent. Employing the method of Cude and Hulett,[14] Knudson[15] found the density of the charcoal to be 1.80; its loss in weight on outgassing is 2.5 percent. The liquids whose vapors were studied were purified by the generally accepted methods.[16] Only the constant boiling middle fractions were used. In all cases the purification was done immediately before the liquid was used. Carbon tetrachloride, chloroform, methylene chloride and methyl chloride were chosen with the hope of observing a possible effect of the number of substituted chlorine atoms on the molecular heat of adsorption.

The method of experimentation, as well as the method of calculating the heats of adsorption, was the same as that described in the previous paper.[6]

The data collected in the experimental work are given in Tables I to VIII. In the first column are listed the final equilibrium pressures. The second column gives the number of cc. of vapor adsorbed by one gram of charcoal. In the third column are the observed heat effects, h_{obs}; while the fourth column contains the values of h calculated by means of the formula given below the Table. The deviations between the observed and calculated heat effects are given in the last column. The data given in these Tables has been obtained with various weights of charcoal, some fresh and others previously used, and with variations in the rate of admission of vapor to the charcoal. The agreement between runs, as well as that within individual runs, indicates that the heat of adsorption is definite and reproducible.

Lamb and Coolidge[3] find that chlorine-containing molecules poison charcoal in such a way that the heat of adsorption decreases in subsequent runs on the same sample of charcoal. This poisoning effect is not evident from our data; the agreement between runs on new and previously used charcoal is entirely acceptable. The heat of adsorption is independent of the previous use of the charcoal provided that it has been outgassed at 550° to a pressure of 0.0001 mm.

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[13] White: J. Am. Chem. Soc., **36**, 2292 (1914).

[14] Cude and Hulett: J. Am. Chem. Soc., **42**, 391 (1920).

[15] Pearce and Knudson: Proc. Iowa Acad. Sci., (1927).

[16] Mathews: J. Am. Chem. Soc., **48**, 562 (1926).

Fig. 3 shows the results obtained when the logarithms of the heats of adsorption are plotted against the number of cc. of vapor adsorbed per gram of charcoal. To avoid overcrowding these curves have been displaced upward by definite increments. The curves are represented mathematically by the expression,

$$\log h = \log m + \log X,$$

where X is the number of cc. of vapor adsorbed by one gram of charcoal, n is the slope of the curve and m is the value of h when X is unity. From the slope of the curve and its intercept on the h-axis we obtained the constants for the equations given beneath the Tables. The values of the heat of adsorption calculated from these empirical equations are in good agreement with the observed values as shown in the last column of each Table.

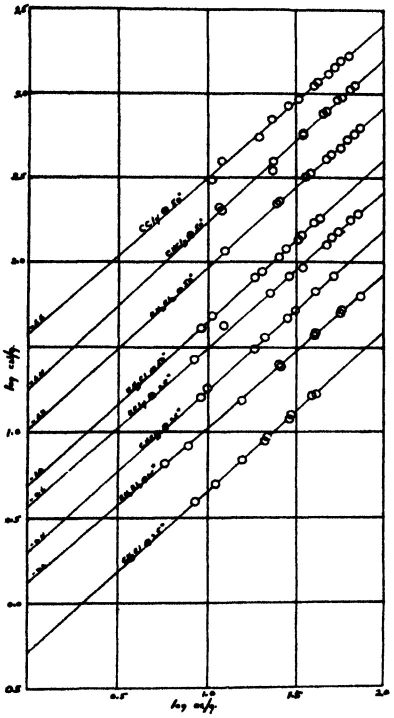

FIG. 3

For the sake of comparison, we have followed the method of Lamb and Coolidge[3] in calculating the molecular heats of adsorption, h_m. Table IX shows the values calculated for the heat of adsorption of a gram molecular weight of the vapor on 500 grams of charcoal. This Table shows also the values of the constants, m and n, of the separate vapors. In all cases the values of n deviate but little from one and are always less than unity. This implies that successive equal increments of a given vapor adsorbed liberate practically the same amount of heat. A comparison of the molecular heats of adsorption of the four vapors at the three temperatures, Table X, indicates that the heat of adsorption is practically constant over the whole range of temperature from 0° to 50°. These results can only lead to the definite conclusion that the temperature coefficient of the heat of adsorption, if there is one, is very, very small.

There is at present no satisfactory explanation for the apparent independence of heat of adsorption and temperature, unless it be that the field forces operative in adsorption processes are too strong to be influenced by the temperature. Lorentz and Lande[17] believe that temperature should have some influence, while Eucken,[18] on the other hand, holds to the view that the heat of adsorption is independent of the temperature. Lamb and Coolidge[3] consider that the observed heat effect is the sum of two effects,—the heat of vaporization of the substance adsorbed and the net heat of adsorption. If the influence of temperature on these two heat effects were equal and opposite in direction, then no observable effect of temperature should be expected. The net heats of adsorption have been calculated, but, owing to the lack of sufficiently reliable density and heat of vaporization data, they are not included in this paper. In general, the heat of vaporization decreases with increasing temperature while the net heat of adsorption increases.

The slopes of the adsorption isosteres have frequently been used in calculating heats of adsorption. It has been shown that these ($\log p - 1/T$) plots yield, in general, straight and parallel lines for a given vapor. If, therefore, the Clausius-Clapeyron equation is applicable to adsorption, no change in the heat of adsorption with rise in temperature should be expected. However, the values obtained by this method are lower than those obtained experimentally.

In the study of the adsorption of chlorine-containing molecules it has been generally assumed that the molecules are oriented with the chlorine atoms toward the surface of the adsorbent. The chlorine atoms possess seven valence electrons in their outer orbits, and the force fields about them should be large. If we may assume that the heat effect observed in adsorption is a result of the neutralization or saturation of the powerful force fields about the surface atoms of the adsorbent, then carbon tetrachloride with its greater number of chlorine atoms should exhibit the greatest heat of adsorption. This is exactly what we do find. From Table X we see at once that for each temperature the molecular heat of adsorption increases with the number of chlorine atoms in the molecule.

TABLE I

The Heat of Adsorption of Methyl Chloride Vapor at 25°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.433	11.17	4.95	4.89	−0.06
1.021	21.01	8.91	8.94	+0.03
1.748	29.11	12.01	12.20	+0.19
3.202	41.34	16.70	17.06	+0.36
1.120	8.57	3.94	3.80	−0.14
2.475	15.79	6.80	6.81	+0.01
3.864	21.79	9.37	9.26	−0.11
5.955	29.66	12.69	12.43	−0.26
9.312	39.08	16.34	16.17	−0.17
			Mean	0.15

$$h = 0.4887\ X^{0.9545}$$

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[17] Lorentz and Lande: Z. anorg. Chem., **125**, 47 (1922).
[18] Eucken: Ber. deutsch. physik. Ges., **12**, 345 (1914).

TABLE II

The Heat of Adsorption of Methyl Chloride Vapor at 50°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.322	9.24	4.08	4.07	−0.01
0.932	18.58	8.12	7.95	−0.17
1.695	25.39	10.71	10.75	+0.04
2.612	32.88	13.87	13.78	−0.09
3.781	39.95	16.99	16.61	−0.38
0.401	10.60	4.80	4.65	−0.25
1.254	20.40	8.76	8.71	−0.05
2.111	27.86	11.97	11.76	−0.21
3.102	34.35	14.43	14.37	−0.06
4.960	43.63	18.08	18.08	0.00
			Mean	0.13

$$h = 0.4820\ X^{0.9600}$$

TABLE III

The Heat of Adsorption of Methylene Chloride Vapor at 25°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.000	7.89	5.23	5.30	−0.07
0.244	25.41	15.80	15.37	−0.43
0.568	41.30	24.17	23.91	−0.26
1.041	57.83	33.13	32.48	−0.65
0.000	5.83	4.12	4.03	−0.09
0.000	15.68	9.65	9.90	+0.25
0.050	25.97	15.25	15.68	+0.43
0.075	40.37	23.07	23.40	+0.33
0.204	57.35	31.61	32.23	+0.62
0.433	74.19	39.97	40.75	+0.78
			Mean	0.39

$$h = 0.8091\ X^{0.9100}$$

TABLE IV

The Heat of Adsorption of Methylene Chloride Vapor at 50°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.124	12.59	7.25	7.36	+0.11
0.302	24.55	13.84	13.79	−0.05
0.610	36.30	20.15	19.92	−0.23
1.070	47.42	25.69	25.61	−0.08
1.660	57.40	29.62	30.65	+1.03
2.602	68.24	36.10	36.05	−0.05
0.000	12.55	7.28	7.34	+0.06
0.074	25.68	14.39	14.39	0.00
0.198	38.78	21.10	21.20	+0.10
0.317	50.44	27.34	27.14	−0.20
0.664	62.29	33.37	33.09	−0.28
1.249	72.75	39.19	38.79	−0.40
			Mean	0.22

$$h = 0.6808\ X^{0.9400}$$

TABLE V

The Heat of Adsorption of Chloroform Vapor at 25°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.000	9.22	6.34	6.33	−0.01
0.000	18.48	12.27	12.30	+0.03
0.025	28.42	18.61	18.56	−0.05
0.030	40.93	26.68	26.31	−0.37
0.060	10.07	7.22	6.89	−0.33
0.164	21.15	14.27	14.00	−0.27
0.244	31.63	20.60	20.56	−0.04
0.413	41.39	26.30	26.60	+0.30
0.692	52.10	32.96	33.14	+0.18
			Mean	0.17

$$h = 0.7569\ X^{0.9560}$$

TABLE VI

The Heat of Adsorption of Chloroform Vapor at 50°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.000	11.58	8.32	7.82	−0.50
0.000	23.66	15.72	15.65	−0.07
0.035	35.00	22.96	22.88	−0.08
0.074	45.53	30.10	29.53	−0.57
0.154	54.90	36.43	35.41	−1.02
0.302	64.85	42.22	41.62	−0.60
0.000	12.13	7.94	8.18	+0.24
0.000	23.48	13.87	15.52	+1.66
0.040	35.04	22.49	22.90	+0.41
0.069	47.62	30.95	30.84	−0.11
0.119	58.84	37.62	37.69	+0.07
0.421	69.29	44.71	44.38	−0.33
			Mean	0.47

$$h = 0.7261\ X^{0.9704}$$

TABLE VII

The Heat of Adsorption of Carbon Tetrachloride Vapor at 25°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.050	12.35	10.53	9.48	−1.05
0.070	29.02	20.78	20.93	+0.15
0.070	47.26	31.59	32.91	+1.42
1.071	61.97	41.72	42.31	+0.59
2.370	64.67	44.41	44.00	−0.41
7.678	71.71	48.05	48.43	+0.38
0.000	8.44	6.68	6.66	−0.02
0.010	22.47	16.51	16.51	0.00
0.086	34.72	22.36	24.72	+1.36
0.494	50.92	34.81	35.26	+0.45
1.915	55.22	38.01	38.01	0.00
			Mean	0.53

$$h = 0.9230\ X^{0.9270}$$

TABLE VIII

The Heat of Adsorption of Carbon Tetrachloride Vapor at 50°

P cm.	X cc/g.	h(Obs) cal/g.	h(Calc) cal/g.	Dev. cal/g.
0.065	10.60	7.68	8.12	+0.44
0.139	18.32	13.76	14.40	+0.64
0.139	28.85	21.11	20.63	−0.48
0.183	40.62	27.85	28.36	+0.51
0.342	48.71	32.77	33.59	+0.82
0.728	63.44	42.00	42.95	+0.95
0.040	12.04	9.92	9.14	−0.78
0.114	23.22	17.59	16.85	−0.74
0.114	33.06	23.34	23.42	+0.08
0.154	42.35	29.31	29.48	−0.17
0.168	52.79	36.00	36.20	+0.20
0.332	57.29	39.18	39.06	−0.12
			Mean	0.49

$$h = 0.9020\ X^{0.9310}$$

TABLE IX

Summary of Calorimetric Data

Substn.	m	n	h_m Cals.
	25°		
CCl_4	0.9230	0.9270	15.6
$CHCl_3$	0.7569	0.9560	14.3
CH_2Cl_2	0.8091	0.9100	12.8
CH_3Cl	0.4887	0.9545	9.2
	50°		
CCl_4	0.9020	0.9310	15.4
$CHCl_3$	0.7261	0.9704	14.5
CH_2Cl_2	0.6808	0.9400	12.1
CH_3Cl	0.4820	0.9600	9.2

TABLE X

Comparison of h_m at 0°, 25°, and 50°

Subs	h_m(0°,L&C) Cals.	h_m(25°, P&McK) Cals.	h_m(25°) Cals.	h_m(50°) Cals.
CCl_4	15.3	15.4	15.6	15.4
$CHCl_3$	14.5	14.5	14.3	14.5
CH_2Cl_2	——	——	12.8	12.1
CH_3Cl	——	——	9.2	9.2

Summary

1. The heats of adsorption of methyl chloride, methylene chloride, chloroform and carbon tetrachloride have been determined at 25° and 50°.

2. The temperature coefficient of the heat of adsorption of the four vapors, if there is one, is very small.

3. The molecular heats of adsorption of the present series increases with increase in the number of chlorine atoms in the molecule.

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THE CATALYTIC DECOMPOSITION OF SODIUM HYPOCHLORITE SOLUTIONS*

III. Promoter Action of Hydrated Magnesium Oxide in the Hydrated Copper Oxide Catalysis of Sodium Hypochlorite*

BY JOHN R. LEWIS

In recent papers,[1] the writer has given the data for the decomposition of sodium hypochlorite solutions in the presence of hydrated copper oxide, used singly, and also in the presence of varying amounts of hydrated ferric oxide. It was shown that the hydrated copper oxide is a fair catalyst for the reaction

$$NaClO \longrightarrow NaCl + 1/2\ O_2$$

It was also shown that small quantities of hydrated ferric oxide, which is not a catalyst for this reaction, greatly increased the activity of the copper catalyst. Such a substance, according to Rideal and Taylor[2] is a promoter.

The investigation has now been extended to include the action of hydrated magnesium oxide. Like ferric oxide, magnesium oxide is not a catalyst for this reaction, but if mixed with the copper catalyst, the activity of the latter is greatly increased.

The particular advantages in studying this problem are:

(1) Catalysts, unpromoted or promoted, can be prepared and used at room temperatures. With many other systems, on the other hand, comparatively high temperatures are required, not only for the preparation of the catalysts, but also for their use in the reactions under investigation.

(2) Duplicate experiments give results which check the original data within experimental error (usually within 2 percent). This places the investigation on a quantitative basis that has not always been realized in other studies in heterogeneous catalysis.

Experimental

Materials and Apparatus.—The sodium hypochlorite and catalysts were prepared according to the methods described in the previous papers. Likewise, the shaker apparatus[3] described in the previous papers was used in following the rate of the reaction.

Experimental Procedure.—The procedure followed in these experiments was essentially the same as that outlined in the second article of this series. The free alkali in the hypochlorite solution was used in precipitating the mixture of copper and magnesium hydroxides. Since, as has been shown by Howell,[4] the hydroxyl ion cuts down the rate of the cobalt peroxide catalysis of sodium hypochlorite solution, it may be argued that the increased catalytic activity of the hydrated copper oxide, in the presence of hydrated magnesium oxide, was due to the removal of hydroxyl ion, by the formation of insoluble magnesium hydroxide. That such is not the case is shown in the following way. Experiments were carried out in which an equivalent quantity of hydrochloric acid was substituted for the magnesium chloride added. This removed the hydroxyl ion by forming water. Typical results are given in Table I.

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* Contribution No. 35 from the Chemical Laboratory of the University of Utah.
Part of the experimental data given in this paper was obtained while the author was connected with the Department of Chemistry of the University of Wisconsin.

[1] Lewis: J. Phys. Chem., **32**, 243-254, 1808-1819 (1928).

[2] Rideal and Taylor: "Catalysis in Theory and Practice" (1926).

[3] Walton: Z. physik. Chem., **47**, 185 (1904).

[4] Howell: Proc. Roy. Soc., **104A**, 134 (1923).

TABLE I

Effect of Removal of Hydroxyl Ion by Hydrochloric Acid

Number of Experiment	Charge	Time in minutes	cc. oxygen liberated
1	10 cc. NaClO	18	0.63
	.003179 g. Cu	35	1.29
	Water to make	122	3.9
	25 cc.	171	5.1
2	10 cc. NaClO	3	1.8
	.003179 g. Cu	12	10.3
	.001216 g. Mg.	24	19.1
	Water to make	40	29.4
	25 cc.	66	41.0
3	10 cc. NaClO	10	0.43
	.003179 g. Cu	25	1.2
	HCl≎.001216 g. Mg.	135	4.4
	Water to make	175	5.6
	25 cc.		

Duplication of Results.—The ease with which results may be duplicated by the experimental method used is illustrated in Table II.

TABLE II

Data for Original and Duplicate Determinations

Original		Duplicate (14 days later)	
Time in minutes	cc. of oxygen	Time in minutes	cc. of oxygen
3	4.1	3	4.4
5	8.5	5	8.8
9	16.8	9	16.7
13	23.9	13	23.7
18	31.4	18	31.2
20	34.2	20	34.0
25	40.4	25	40.2

Results

The results obtained are summarized in Table III and shown graphically in Fig. 1. The value for K_1, the unimolecular constant, is that obtained when the hypochlorite in each determination is 20 percent decomposed.

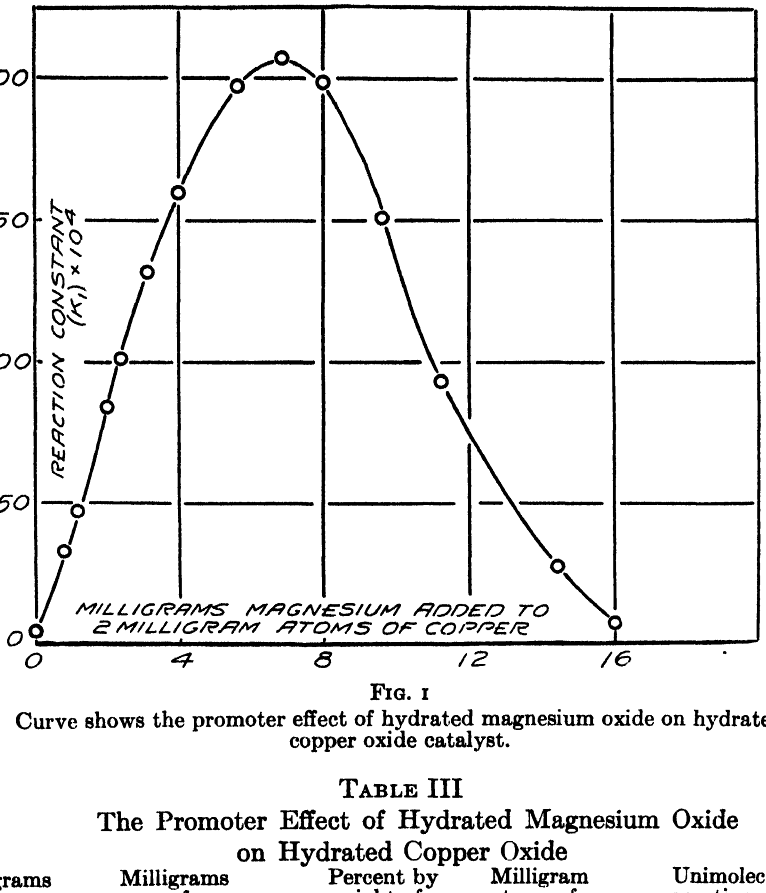

FIG. 1

Curve shows the promoter effect of hydrated magnesium oxide on hydrated copper oxide catalyst.

TABLE III
The Promoter Effect of Hydrated Magnesium Oxide on Hydrated Copper Oxide

Milligrams of copper per liter	Milligrams of magnesium per liter	Percent by weight of magnesium in catalyst mixture	Milligram atoms of magnesium added to two milligram atoms of copper	Unimolecular reaction constant $K_1 \times 10^4$ at 20% decomposition
127.1	0	0	0	3.5
127.1	19.45	13.27	0.8	31.3
127.1	29.2	18.68	1.2	46.8
127.1	38.9	23.2	1.6	72.3
127.1	48.6	27.7	2.0	84.5
127.1	58.3	31.4	2.4	100.5
127.1	77.0	37.7	3.17	132.0
127.1	97.3	43.3	4.0	160.0
127.1	136.0	51.7	5.6	197.0
127.1	165.0	56.5	6.78	207.0
127.1	194.1	60.4	8.0	198.0
127.1	233.5	64.7	9.6	150.0
127.1	272.2	68.3	11.2	93.9
127.1	350.2	73.5	14.4	27.0
127.1	389.0	75.4	16.0	8.34

Discussion of Results

Examination of the data in Table III or the curve in Fig. 1 shows:

1. The maximum promotion of the copper catalyst, under the conditions of these experiments, is reached when the ratio of copper atoms to magnesium atoms is one to three or four.

2. When the ratio of copper to magnesium is one atom to eight atoms, the promoter effect has practically disappeared.

These experimental results may be accounted for by assuming that the promoter aids in the *formation* and *preservation* of active centers on the catalyst particles. It was suggested, in the second article of this series, that the fall in the activity of the unpromoted copper catalyst was due largely to a reduction in the number of active centers, through the agglomeration of the catalyst particles. On the other hand the suitably promoted catalyst maintained its activity due to the *prevention* of *agglomeration* of the particles. Evidence in support of such an assumption is now presented.

The unpromoted hydrated copper oxide catalyst, in these experiments, is blue when first precipitated, but soon changes to a dark brown or black. Weiser[1] states that the blue hydrated copper oxide is more finely divided than the black variety and that the black may be formed from the blue through the coalescence of the particles. The work of Schenck,[2] in Bancroft's laboratory, showed that the blue copper oxide may be ignited without undergoing a change in color if sufficient aluminum hydroxide is present to prevent 'sintering'. In the work in this laboratory, it was observed that in the most actively promoted catalyst, the hydrated copper oxide *remained* blue. In those catalyst-promoter mixtures where the ratio of copper to magnesium atoms was one to ten, twelve or more, the mixture was white, showing that the copper compound was largely covered with the hydrated magnesium oxide. Here, it will be observed, the promoter effect is very slight.

In an important investigation, it has been shown by Frankenberger and Mayrhofer[3] that an iron catalyst for the ammonia synthesis, may be maximally promoted by depositing single iron atoms on a surface in such a way that they cannot coalesce. This was accomplished by spraying a mixture of iron atoms and water molecules, in the ratio of one iron atom to four water molecules, onto a surface cooled with liquid air. It was found that the iron atoms combined with hydrogen molecules in the ratio of one to one. In the experiments described here, the promoter has the same function (at least in part) as in Frankenberger's experiments. In his, the water molecules prevented the coalescence of the iron atoms; in the experiments described here, the magnesium oxide prevented the coalescence of the copper oxide particles. It is not unreasonable to suppose that the ideally promoted hydrated copper oxide catalyst is one in which each molecule is separated from its neighbors by a definite number of molecules of the promoter. It seems reasonable to suppose that those oxides or hydroxides whose crystal structures are the same as those of the catalyst oxides should have the property of separating the catalyst molecules from each other in a definite manner, say by forming mixed crystals, and thus becoming the best promoters. It is the intention of the author to make future studies approaching the problem from this point of view.

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[1] Weiser: "The Hydrous Oxides" (1926).

[2] Schenck: J. Phys. Chem., 23, 283 (1919).

[3] Frankenberger and Mayrhofer: Z. Elektrochemie, 35, 590 (1929).

Summary

1. The promoter effect of hydrated magnesium oxide on the hydrated copper oxide catalysis of sodium hypochlorite has been studied. The data obtained are given in tables and shown graphically.

2. The maximum promoter effect is obtained in those mixtures of catalyst and promoter where the ratio is one atom of copper to about four atoms of magnesium.

3. In the most effective catalyst-promoter mixtures, the color of the hydrated copper oxide remains blue. This shows that the promoter preserves the activity of the catalyst through the prevention of the agglomeration of the particles.

Salt Lake City, Utah.

NEW BOOKS

Crucibles. *By Bernard Jaffe. 24 × 17 cm; pp. ix + 377. New York: Simon and Schuster, 1930. Price: $5.00.* This book contains interesting sketches of Bernard Trevisan, Theophrastus Paracelsus, John Joachim Becher, Joseph Priestley, Henry Cavendish, Antoine Laurent Lavoisier, John Dalton, John Jacob Berzelius, Amedeo Avogadro, Friedrich Woehler, Dmitri Ivanovitch Mendeléeff, Svante Arrhenius, Marie Sklodowska Curie, Joseph John Thomson, Henry Gwyn Jeffreys Moseley, and Irving Langmuir.

"Some of the apparatus and utensils which are the tools of the chemist of our scientific laboratories were first introduced by alchemists—cupel, distilling flask, retort, water bath and even the balance in its crude form. The extraction of gold by amalgamation with mercury, the preparation of caustic alkali from the ashes of plants, and other new processes of manipulation and methods of manufacture were developed by the gold cooks in their manifold operations," p. 16.

"The world owes bombastic Paracelsus a great debt. This revolutionist with the imagination of a poet and the fearlessness of a crusader, was much more than the bibulous braggart his enemies had called him. He was a real benefactor of mankind. His great contribution was no one epoch-making discovery, but rather the vital impetus he gave to the study of chemistry for the curing of ills of the body. He swept aside the teachings of the ancient authorities and brought alchemy to the aid of medicine," p. 30.

"Becher introduced the potato into Germany to feed its swine and cattle and to prevent famine among the poor. He patented a method of distilling coal. He started work on a lamp that would burn forever. He invented weaving and spinning machines. Various mining and metallurgical processes were devised by him. They all ended in commercial disaster. But in spite of his many bankruptcies, there was something about Becher that kept the believing world ready to listen to him once more. His fame as an economist had spread. In 1664 he was called to Mannheim to introduce new manufactures. He was to be given a free hand in the development and enrichment of the city. He planned a new era in the industrial life of that city. He outlined projects for the introduction of the manufacture of glass, paper, and even silk. Silk for the looms was to be obtained from a silk-raising industry which he was to inaugurate. It was an ambitious undertaking," p. 45.

Priestley became interested in the gas which bubbles off in the huge vats during the process of beer-making. "Unable to obtain sufficiently large quantities of this gas from the brewery, he learned to prepare it at home. He tried dissolving the gas in water. It was not very soluble, but some of it did mix with water. In this manner in the space of two or three minutes he made, as he related, (a glass of exceedingly pleasant sparkling water which could hardly be distinguished from Seltzer water.) Appearing before the Royal Society he told that learned body of his discovery of what we now know as soda water—a very weak acid solution of carbon dioxide gas in water. The Royal Society was intensely interested, and he was asked to repeat his experiments before the members of the College of Physicians. He jumped at the opportunity, and as he bubbled the gas through water, he asked some of those present to taste the solution. They were very much impressed, and recommended it to the Lords of the Admiralty as a possible cure for sea scurvy. Priestley received the Society's gold medal for this discovery, the first triumph ot this amateur chemist in science," p. 56.

"Cavendish obtained six samples of gas by the action of hydrochloric acid and of sulphuric acid on zinc, iron and tin. "The experimenter now brought a lighted taper to his six samples of gas. He watched each specimen of gas burn with the same pale blue flame. Strange that the same gas should be evolved in each case! What else could this inflammable air be, but that elusive phlogiston? For had not Becher taught that metals were compounds of phlogiston and some peculiar earths? Surely Cavendish had proved that the gas came, not from the acids or water in the bottles, but from the metals themselves! But he must not announce this until he had investigated further—it would not do to startle the world before he had made certain he was right.

"With the crude instruments at his disposal, he passed the gases through drying tubes to free them of all moisture, and then he weighed the pure imprisoned "phlogiston." Though extremely light he found it actually had weight. It was ponderable. He had nailed phlogiston itself! Now, at the age of thirty-five, he published an account of this work on "Factitious Airs" in the Transactions of the Royal Society," p. 76.

"Lavoisier was a careful worker with an idea at the back of his head which grew clearer as he read or repeated the experiments of his predecessors and contemporaries. Slowly he began to weed out the faulty explanations and weak theories that had crept into chemistry. Phlogiston did not fit into his scheme of chemistry. While the rest of Europe clung to it tenaciously he could see through it. To him it was a myth, an idle mischievous theory with neither foundation nor substance. There must be a simpler and more logical explanation of burning than Becher's phlogiston. With the coolness and dexterity of a skilled surgeon, he began to dissect the old idea. The creature was rotten to the core.

"With scientific intuition he rejected this theory before he had thought of a substitute, but he was going to find an alternative. This practical Lavoisier who, at twenty-two received a gold medal from the Academy of Sciences for working out the best method of lighting the streets of Paris; this same Lavoisier who, before submitting his essay, had worked for months on this problem, shutting himself up in a dark room for six weeks to render his eyes more sensitive to different lights; he was going to find the true explanation of burning! Phlogiston would not do," p. 102.

"Suddenly, after deep thought, the whole atomic theory was revealed to him [Dalton]. He did not wait for experimental verification. Like Galileo, he did not feel that experimental proof was always absolutely essential. Like Faraday, he possessed, to an extreme degree, a sense of physical reality. Dalton, cat on his knee, began to draw pictures of his atoms," p. 122.

"Berzelius began to work with his oldest half-brother, Lars Ekmarck, on voltaic electricity. His thesis for his medical degree was on the action of electricity on organic bodies. The following year, with his friend, von Hisinger, he published a paper on the division of compounds by means of the voltaic pile, in which he propounded the theory that metals always went to the negative pole and non-metals to the positive pole of the electrical machine. Benjamin Franklin had introduced this idea of positive and negative electricity. He had called a body positively electrified when it could be repelled by the glass rod rubbed with silk.

"The work of Berzelius, however, hardly caused a ripple in the chemical stream of progress. But four years later a young chemist in England, reading an account of his works and following them up, fired the imagination of the world. Benjamin Franklin had 'disarmed the thunder of terrors and taught the fire of heaven to obey his voice,' but now Humphry Davy, using Volta's electric pile and the research of Berzelius, isolated such new and strange elements as staggered men even more than the discovery of phosphorus a century before," p. 143.

"A firm believer in the atomic theory of Dalton, Berzelius made his new symbols stand for the relative atomic weights of the atoms. The initial letter capitalized represented one atom of the element. These symbols stood for definite quantitative measurements and 'enabled us to indicate without long periphrases the relative number of atoms of the different constituents present in each compound body.' Thus they gave a clew to the chemical composition of substances. This was a tremendous step toward making chemistry a mathematical science," p. 147.

"Not a word of eulogy was pronounced at Avogadro's simple bier. Only brief obituaries appeared in a few scattered scientific journals filled with accounts of the discovery of the first skeleton of a Neanderthal man; of mauve, the first coal tar dye discovered by Perkin in Hofmann's laboratory in London; of a blast furnace for making steel designed by

Bessemer. Not a single word about his monumental memoir of the molecules—a glaring example of the neglect of genius.

"When a bust of Avogadro was unveiled a year after his death, not a chemist was there to utter a word of homage. Even in his own country he was little known. Only two of his pupils, both physicists, recalled his work. His classic theory of the molecules had appeared originally not in Italian but in French. It was later translated into both German and English, and, although most incredible, was not available in his own language until the opening of the twentieth century. So extremely modest and retiring was this Italian professor that, great as were his contributions in the field of science, when the Scientific Congress met in his own native city, he was not even nominated an officer of that body," p. 166.

"When Woehler was sure of his ground, he wrote to Berzelius, 'I must tell you that I can prepare urea without requiring a kidney of an animal, either man or dog.' The Swede enthusiastically spread the news. The world of science was electrified. Chevreul hailed the achievement with joy. Woehler had actually synthesized urea out of inorganic compounds! What was to prevent others from building up the sugars, the proteins, perhaps even protoplasm, the colloidal basis of life itself? A feeble protest still sounded from the vitalists. Urea was perhaps midway between the organic and inorganic world. For to make urea one must use ammonia which originally was of organic origin. The vital force present in organic substances never disappeared and consequently was capable of giving rise to other organic bodies. So they argued. But even that whisper was soon lost in the great tumult of excitement. It was indeed a brilliant new day for chemistry," p. 177.

"Out of Russia came the patriarchal voice of a prophet of chemistry [Mendeléeff]. 'There is an element as yet undiscovered. I have named it eka-aluminum. By properties similar to those of the metal aluminum you shall identify it. Seek it, and it will be found.' Startling as was this prophecy, the sage of Russia was not through. He predicted another element resembling the element boron. He was even bold enough to state its atomic weight. And before that voice was stilled, it foretold the discovery of a third element whose physical and chemical properties were thoroughly described. No man, not even the Russian himself, had beheld these unknown substances," p. 199.

"In the historic chemical laboratory of the University of Leipzig two men, a German born in Riga, and a Swede, met towards the end of the nineteenth century to plan a great battle against an established theory and the scientific inertia which upheld it. Meanwhile, over in Amsterdam, another scientist, a Dutchman, worked in the same campaign. From this triumvirate came a barrage of scientific experiments which made possible a new era in the field of theoretical and applied chemistry. Here, at Leipzig, the Headquarters of the Ionians, the great struggle was directed.

"The three were all young men. Svante Arrhenius was hardly more than a boy. Van't Hoff, the Dutch professor, was thirty-five, and Ostwald, the moving spirit of the revolt, a year younger. The quest for scientic truth had brought these three together, and they vowed to force the venerable authorities of the scientific world to accept the new leaven of the younger generation. The masters, under whom they had cut their scientific eyeteeth, must be shown the folly of ignoring genius among their students," p. 219.

"A strange element had been discovered by a woman. Its salts were self-luminous; they shone in the dark like tiny electric bulbs. They were continuously emitting heat in appreciable quantities. This heat given off was two hundred and fifty thousand times as much as that produced by the burning of an equal weight of coal. It was calculated that a ton of radium would boil one thousand tons of water for a whole year. This new element was the most potent poison known to mankind—even acting from a distance. A tube containing a grain the size of a pinhead and placed over the spinal column of a mouse paralyzed it in three hours; in seven hours the animal was in convulsions and in fifteen hours it was dead. Radium next to the skin produced painful sores. . . . Its presence sterilized seeds, healed surface cancer and killed microbes. It colored diamonds and the glass tubes in which it was kept. It electrified the air around it, and penetrated solids.

"The world marveled at the news. Here was another one of nature's surprises. Chemists were bewildered. A woman had not only pushed back the frontiers of chemical knowledge—she had discovered a new world waiting to be explored. From every laboratory on the face of the earth came inquiries about this magic stone. The imagination of the world was kindled as by no other discovery within the memory of man. Overnight the Curies became world famous," p. 255.

"Three eminent scientists constituted the Board of Electors which was to make the final choice—Lord Kelvin, the Scotchman who in Glasgow worked out the intricate problems of the first Atlantic Cable; Sir George Gabriel Stokes, investigator of fluorescence; and Professor George Howard Darwin, second son of Charles Darwin. They saw inside that massive head of Thomson an imaginative yet crystal-clear mind with powerful penetrating power. The lad from Manchester was chosen. 'Shades of Clerk-Maxwell,' declared one well-known professor. 'Things have come to a pretty pass in the University of Newton when mere boys are made professors.' Michael Pupin, the eminent American scientist, coming from a cracker factory in New York to study physics under Clerk-Maxwell at Cambridge was frightened away when he learned that a young lad, only two years his senior, had been put at the head of the famous Cavendish Laboratory. 'I thought he was too young to be my teacher of physics,' he complained.

"And so it came about that a mere boy filled the chair to two illustrious predecessors, and under his leadership the Cavendish Laboratory became the dominant center of scientific research in the world. Here was carried on more important research per square foot than in any other part of the earth. Here men's minds soared to heights never dreamed of before. The spirit of the boy Thomson was to pervade that sanctum of science for nearly half a century," p. 266.

"In 1912, at the age of twenty-six, Moseley published his results—he had discovered the Law of Atomic Numbers. He prepared a new Table of the Elements more fundamental than that of his Russian predecessor. He gave the world an infallible road map of all the elements of the universe—a chart based, not on atomic weights, but on atomic numbers. Mendeléeff's romantic blue-prints had served science for fifty years. Now a new and more enduring structure was reared, fashioned by the cunning brain of a youth," p. 298.

"Atoms, said Langmuir, differ from each other in chemical activity only because of their tendency to complete their outside shells and thus render the atom stable. Argon, the third inert gas in Moseley's Table of Elements, has an atomic number of 18. Its first shell is complete with two electrons, its second shell is also complete with eight additional electrons, while its third shell likewise contains eight electrons, showing once more a stable configuration. Hence argon is inert. Chemical affinity is thus a condition dependent upon the nature of the outermost shell electrons. When the outside shell of an atom contains very few electrons, its tendency is to lose them. Such an atom is a metal. If, on the other hand, the outermost shell of an atom contains an almost complete ring, it will strive to borrow some electrons from other atoms which are anxious to lose them. Such an atom is a non-metal. Metals are lenders of electrons and non-metals are borrowers. Hence metals and non-metals will combine energetically with each other and both, by an exchange of electrons, assume the stable condition. Chemical affinity or union, therefore, depends upon this transfer of electrons. In a polar union a positive atom loses its valence electrons to a negative atom and the two atoms are held by electrostatic attraction. In a non-polar union electrons are not actually transferred—the two atoms approach each other so that one or more valence electrons of one atom occupy the vacant positions in the valence shell of the second atom. Octets are thus formed by a process of sharing electrons," p. 329.

Cannizzaro's name is misspelled consistently and so are one or two others. It is only by a stretch of the imagination that one can call Moissan the inventor of the electric arc and Lippman the developer of color photography, p. 254.

Wilder D. Bancroft

The Wave Mechanics of Free Electrons. *By G. P. Thomson. 23 × 16 cm; pp. 172. New York and London: McGraw-Hill Book Company, 1930. Price: $2.50.* Professor Thomson was the George Fisher Baker non-resident lecturer at Cornell University during the Fall term of 1929. In his introductory lecture on "Waves and Particles," the author says: "Atoms can be made to emit light, and each atom emits its own characteristic wave-lengths. These are clearly a consequence of the structure of the particular atom, presumably of the arrangement of its electrons. Now one theory, and one only, was found capable of explaining these wave-lengths even in general terms. This was the theory due to Niels Bohr according to which the electrons were supposed to move in orbits round the nucleus rather like planets round the sun. But in order to make the theory fit the facts, Bohr had to assume a behavior of the electrons which is quite contrary to ordinary dynamics, and curiously enough the same quantity *h* came in, though in quite a different way. The real trouble was not so much that the electrons obeyed laws different from those of Maxwell and Newton, but that they were not consistent about it. Some of the things they did required the old laws to explain them; others required a new and inconsistent set. Sometimes both had to be used in different parts of the same calculation. The position of a physicist investigating an atom was rather like that of a man trying to make sense of an account of a game which started as golf and suddenly for no apparent reason turned into tennis and then back to golf again. Worse still, as time went on it became clear that the electrons did not play fair even at the game they had for the moment chosen. The results were nearly right but not quite. The only hint was that the quantity *h* came in whenever the atom chose to break the old rules, and this suggested a connection with the photo-electric paradox. The first really successful attempt to solve these difficulties is due to Prince L. de Broglie. He realized that the reason why the electron in the atom seemed to follow two different sets of rules at once was that it was behaving much more like a wave than a particle. Now if you think that you are reading of an account of a game played with a ball, when really the reporter was writing about a swimming match, it is not to be wondered at if the report does not make good sense. It is perhaps surprising that the physicists made as much of it as they did. De Broglie's theory was a mathematical one based on relativity. He reached the conclusion that any moving particle would be accompanied by a wave, and he postulated that this wave controlled the motion of the particle. Instead of Newton's laws of motion (motion in a straight line, acceleration proportional to the force, and so on) this view gives a motion governed by waves. Of course Newton's laws are true in every-day life. This is because a very short wave is indistinguishable in behavior from a particle, and the scale of de Broglie's waves is given by *h*, which is a very small quantity. But according to his theory the smaller the particle the longer the wave. For an electron in an atom the wave is quite comparable with the size of the atom, and the behavior of the electron is greatly different from what you would expect of a particle. It has been found, in fact, that this theory when fully applied mathematically, as it has been by Schrödinger and others, brings order out of chaos in the explanation of the properties of atoms," p. 6.

"A question that inevitably arises is: What is the medium which transmits electron waves? I am sorry that I can give no entirely satisfactory answer. For the first time, physics is faced with waves in empty space which do not fit into the ordinary series of ether vibrations. All the ether vibrations differ only in wave-length; if the wave-length is given, the kind of 'light' is fixed. The electron waves have varying wave-lengths depending on the speed of the electron, but they usually fall in a region of wave-lengths which is already appropriated by X-rays. As we have seen, they are certainly not the same as X-rays. One must suppose some other medium, or at least that the ordinary ether is in some way profoundly modified by the presence of the electron. It is possible that they are waves in a 'subether.' But it is not a very attractive idea to have two ethers filling space, especially as the waves of protons—if they exist—would demand a third. Space is becoming overcrowded. Other suggestions are to regard the waves as a kind of mathematical abstraction, a sort of ghost waves. The whole question is getting very metaphysical," p. 11.

The chapters are entitled: general theory of waves; De Broglie's wave mechanics; theory of wave diffraction by crystals; the experimental evidence; effect of a continuous medium on the waves; interaction between electrons and atoms; theoretical interpretation; physical theory; the magnetic properties of the electron; applications of electron diffraction.

"The results of the transmission experiments may be approximately explained by the following assumptions:

"(1) Each electron is associated with a wave of approximate wave-length h/mu, the length of the train being at least 50 waves and the breadth in the wave front at least 30×10^{-8} cm. in certain cases.

"(2) Each atom of the crystal is the center of a wavelet coherent with the original wave, and whose intensity varies with the angle to the original direction of motion of the electron, in a manner which can be calculated from the distribution of charge in the atom (p. 115).

"(3) The chance of the electron appearing at any place with its original energy is proportional to the intensity of the composite wave formed by the wavelets.

"It should be noticed that the electron is detected by any of a number of processes, such as the charging of a Faraday cylinder, the development of the grain of a photographic plate, or a scintillation on a screen, all of which can be interpreted only as the arrival of a particle with a certain charge and energy.

"(4) There is also a chance of the electron losing energy in passing through the crystal. In this case its deflection is governed by other laws of which little is known at present.

"The discrepancies between the above theory and the reflection experiments at low voltage apparently can be explained by considerations of the type presented at the end of Chapter V, which involve the investigation of the interaction of a wave train with the complicated periodic distribution of potential in the crystal. On this view assumption (2) is a convenient approximation to the result which should be obtained by a rigorous solution of Equation (5), p. 29, using for F the actual distribution of potential throughout the crystal. Mott's calculation of the scattering of single atoms also fall into line with this view.

"It seems, then, that we may regard the reflection experiments as accounted for by assumptions (1)-(4) above, if they are modified in the sense that the chance of an electron appearing is to be taken as proportional to the intensity of the scattered waves which satisfy Equation (5), page 29, using a value of F determined by the structures of the crystal and of its component atoms.

"It should be emphasized that, at least so far as present knowledge goes, the behavior of any particular electron must be expressed in terms of probability. For example, in a transmission experiment there is no way of knowing in advance whether any given electron will appear in the central spot or on a ring, and the same difficulty would arise even if the crystal were large and there were only one Laue spot to which diffraction could occur. In addition, there is always a probability of inelastic collision. It seems possible, however, at least in theory, to regard each electron as an individual particle fastened in such a way to a wave system obeying Equation (5), page 29, that it always moves along the wave normal. The expression for the necessary velocity has been given in practically equivalent forms by de Broglie and Schrödinger," p. 119.

"Towards the end of the history of the orbit theory of spectra it became apparent that a simple point electron was inadequate to explain the observed facts. To take only one difficulty, it was found that four quantum numbers had to be assigned to each electron. Now each quantum number may be regarded as fixing one degree of freedom, and a point has only three of these. This and other difficulties were overcome by Goudsmit and Uhlenbeck who suggested that the electron was to be regarded as a spinning body whose axis of spin could vary. Actually it was only necessary to suppose two possible directions for the axis, or rather one direction associated with a spin of either sense. One could think of the axis, for example, as always perpendicular to the oribt and the electron as spinning with or against its orbital motion. Such an electron would be expected to behave like a small magnet, and it was found in fact that agreement with experiment resulted if the moment was taken as $eh/4\pi mc$. This value fits in with the results of the Stern-Gerlach experiments.

"Nothing in the preceding theory at all corresponds with this conception of the electron as a magnet to whose axis a definite direction in space is to be assigned, and it is not surprising, therefore, that the theory in this form should fail to account for those facts which made the hypothesis of the spinning electron necessary on the older theory. The necessary extension of the equations to cover this aspect of the electron has been made by Dirac, using the methods of non-commutative algebra; his results have been expressed in more ordinary form and considerably extended by Darwin whose methods we shall follow," p. 141.

Wilder D. Bancroft

Katalyse. *By W. Frankenburger and F. Dürr. 27 × 19 cm; pp. 58. Berlin: Urban and Schwarzenberg, 1930. Price: 3.50 marks.* This pamphlet is a reprint of the article on catalysis in the second edition of Ullmann's "Enzyklopaedie der technischen Chemie." The authors are in the research laboratory of the I.G. at Oppau. They are quite frank about admitting that there is no prospect at present of being able to predict theoretically what will be the best catalytic agent for any particular reaction, pp. 3, 30.

The authors group catalytic reactions under ten heads, p. 19:—

1. Hydrogen ion is often effective in causing addition of splitting off of water.

2. Hydroxyl ion is often effective in causing condensations, polymerizations, and racemizations.

3. Substances which can occur easily with two valences are often effective in causing oxidations.

4. Hydrogenations in presence of hydrogen gas are helped by presence of platinum, palladium, rhodium, nickel, cobalt, iron, and copper.

5. The splitting-off of water from the vapors of organic substances is facilitated by the oxides and phosphates of thorium, aluminum, and tungsten; also by kaolin which the authors for some unknown reason call bauxite.

6. Condensations in organic chemistry are often speeded up by metallic chlorides.

7. The introduction of carbon monoxide into an organic hydrocarbon can be done in presence of a mixture of hydrochloric acid with aluminum or cuprous chloride.

8. Halogenations are catalyzed by chlorides, iodine, sulphur, and charcoal.

9. Cuprous salts or copper powder favor the substitution of halides for the diazo group.

10. Cracking of hydrocarbons is catalyzed by aluminum chloride, metals, and active carbon.

The authors postulate the intermediate formation of something not necessarily a compound according to the laws of definite and multiple proportions, p. 27. This is of course perfectly safe, and absolutely useless. It is worse than useless because they think that they have said something and are therefore not especially interested in what actually happens in any particular case. They admit the existence of negative catalyzers which break up a chain reaction; but they do not believe in the existence of what people usually mean by negative catalyzers, p. 36.

The authors cite, p. 47, the work of Hoover and Rideal in which thorium causes the splitting-off of hydrogen from alcohol when the catalyst is poisoned by water and the splitting-off of water when the catalyst is poisoned by chloroform. This would seem to imply that the work of Adkins with catalysts made from aluminum ethylate for instance was affected by poisons, as suggested by H. S. Taylor. Experiments to decide this point are now being carried out in the Cornell laboratory. The belief is expressed, p. 50, that, with the nickel-molybdenum alloy for the synthesis of ammonia, the nickel activates the hydrogen and the molybdenum the nitrogen.

The last paragraph, p. 58, is especially interesting as coming from two industrialists. "A glance over the technical catalytical processes developed so far shows the extraordinarily manifold applications of the contact processes as time-savers in producing chemical products of the most varied nature. In spite of the number of catalytic industrial processes, they are far removed, economically and in changing the course of the reaction by gentle means, from what living nature shows us daily as a symphony of catalytic processes. In vegetable and animal organisms—without use of powerful reagents such as high gas pressures or high temperatures—there occur most remarkable catalytic reactions in harmonious interlocking. Homogeneous and microheterogeneous catalyses take place under the influence of inorganic and organic catalysts; also reactions at surfaces which under the influence of the sun's rays convert chemically inert gases like carbon dioxide into compounds with high molecular weights; and processes by which the complicated substances of the vegetable and animal organisms are built up with ease from the simplest components. Most of these reactions have not even been studied yet in spite of all that has been done. It can be predicted that the industry of the future will have to model itself more than ever before on nature in order to exhaust the possibilities to come from the study and mastery of catalytic phenomena.

Wilder D. Bancroft

The Spirit of Chemistry. *By Alexander Findlay. 22 × 15 cm; pp. xvi + 480. London and New York: Longmans, Green and Co., 1930. Price: $3.50; 10 shillings, 6 pence.* "This book", the author states, "has been written as a text-book for those students, more especially, who, in the Universities of Great Britain and in the Colleges of the United States, in increasingly large numbers, pursue a course in chemistry as an element of general culture rather than as a part of their professional or technical training." This difficult task is one to which Professor Findlay has given much consideration and in which he made a beginning fifteen years ago by the publication of his well-known "Chemistry in the Service of Man". The scope of the present work is however much more comprehensive and in the twenty-nine chapters we have a display of the science in a great multitude of its implications with thought and life. The interest of the book is heightened by the blending of the history and philosophy of the science with a very carefully selected range of information on matters both abstract and concrete likely to interest a student of healthy intellectual appetite. The intercalation of biographical notices, the abundant and clear accounts of the industrial applications of chemistry, and the wealth of fine illustrations greatly enlighten the narrative.

To say more about the detail of the book is unnecessary; it can be confidently affirmed that it is an extremely interesting exposition of chemical science and its applications, reflecting the philosophic mind of a chemist thoroughly abreast of the times. It is a book that may surely be read with profit by chemistry students in general.

There remains the question how far Professor Findlay has accomplished the particular task to which he set himself as indicated by the title and sub-title of his book. There is no doubt an increasing demand from those concerned with what Professor Findlay calls "the liberal arts"—broadly speaking literary studies—that their curriculum shall include some measure of natural science. It is also a matter of great concern to science that the demand should be met. It is an exceedingly difficult question, and one on which we cannot expect to speak with confidence until much further experience has been gained. We are at the present day in a state of educational transition. Education is always changing, but there can be no doubt that the world-shaking discoveries and achievements of science of the last 20 years have shaken even the most somnolent or disdainful sections of thinking men into a lively conviction that science counts and is going to count immensely for good or evil. We may put the awakening no higher than a realisation that science has to be reckoned with and that to reckon with it you really will have to get to know a little more about it.

There is however this great difficulty that custom has so long sanctioned the neglect of science as a normal part of a liberal education that in those who come to universities for literary studies we cannot for the time being assume that they have learned even the ABC of natural science. We are really called upon to do with mature minds in a university what should have been done upon the child mind in school.

The bearing of these observations upon Professor Findlay's book is that they raise the question, first, whether he has not provided too rich a table of chemical erudition, and, secondly, what place does he give to the craftsmanship of chemistry in his scheme, that is, to laboratory work and the actual practice of the experimental method. To the second question Professor Findlay has kindly replied in private correspondence. As was to be expected he is strongly in favour of practical work being pursued; he believes that "it is absolutely essential for the full development of the scientific spirit" and as a matter of fact he requires it of all his students. But he alludes to the time difficulty, which all will acknowledge, and on the principle of half a loaf being better than no bread, he feels that "a suitable lecture course would prove of great value to an Arts student even if he does no laboratory work at all."

The writer of this notice has been sufficiently concerned with the problem to know its difficulty and to refrain from laying down the law. He has consorted with those who believe that inasmuch as the primary and distinctive power of science lies in the experimental method, it is a comprehension of this above all else that we should try to impart to those who come late even with small pitchers to our wells. He is convinced that to attain this end the actual practice of the science is indispensable. And so whilst believing that a course of experimental lectures given by teachers like Professor Findlay—a scarce kind it is to be feared—would be invaluable, he would himself be content to make a greater sacrifice of substance to method than the author has made in this interesting book.

Arthur Smithells.

Errata

Owing to the proof not having been read by the author and to errors in the manuscript, some corrections must be made in the paper by Maurice Lecat: **34**, 2508 (1930).

p. 2508 line 28, read azeotrope A for azotropea.

p. 2511 line 18, read Chavanne instead of Chaname.

p. 2511, footnote 19, read unicity for constancy, phenyldiimine for phenyldiamine, and cyclohexane for cyclohexene.

p. 2512 line 21, read eutectism for eutexi.

p. 2513 line 6 from bottom, read $Z\sim$ either to zero or instead of or.

p. 2514 line 3, read nature instead of mixture.

p. 2514 line 11 from bottom, read $\sim$ instead of M.

p. 2515 line 2, read $|\delta|$ instead of $1\delta|$.

p. 2516 line 4, read L instead of to.

p. 2516 line 9 from bottom, read apparatus instead of approach.

p. 2517 line 12, read two instead of four.

p. 2517 line 18 from bottom, read missing instead of mixing.

p. 2517 line 1 from bottom, read small instead of final.

p. 2518 line 14, read step instead of X-step.

Errata

Owing to the proof not having been read by the authors and to errors in the manuscripts, some corrections must be made in the papers by Messrs. Miles and Milbourn and Miles and Craik: **34**, 2598, 2607 (1930).

p. 2602 Fig. 4, read 7.10% for 71.0%.

p. 2603 line 12, read solution for swelling.

p. 2604 line 2, read No. 20 for No. 42.

p. 2604 line 6, read nitrating acid for nitrating.

p. 2604 line 16, read Fig. 1 instead of Fig. 7.

p. 2606 line 22, read Mr. T. Donaldson instead of Mr. J. Donaldson.

p. 2606 line 23, read Dr. J. Weir instead of A. J. Weir.

p. 2607 line 30, read portions for positions.

p. 2608 line 32, read advisable at 0° for advisable at 20°.

p. 2609 line 8, read or mercerised for of mercerised.

p. 2610 line 2, read of them for of the.

p. 2613 line 1, read solution for swelling.

p. 2613 line 3, read condition for conditions.

p. 2616 line 3, read small definite for shall definite.

p. 2620 line 8, read solution for swelling.

p. 2620 line 21, read Mr. T. Donaldson instead of Mr. J. Donaldson.

p. 2620 line 22, read Dr. J. Weir instead of Mr. J. Weir.

A PORTION OF THE SYSTEM, FERRIC OXIDE-CUPRIC OXIDE-SULPHUR TRIOXIDE-WATER

BY G. TUNELL AND E. POSNJAK

Introduction

The investigation of the system, ferric oxide-cupric oxide-sulphur trioxide-water, was undertaken primarily to gain some knowledge of the processes which take place and the equilibria which may be attained during the natural oxidation of the disseminated iron and copper sulphide ore bodies in altered porphyry. Since these processes presumably take place in the neighborhood of surface temperatures and in not very concentrated solutions, the investigation was restricted to these conditions as it would have required a very large amount of time to work out the quaternary system completely.

Experimental Methods

For the preparation of the initial mixtures, besides normal cupric sulphate and normal ferric sulphate, a basic ferric sulphate and a specially prepared suspension of cupric oxide together with the required amount of water were used. The basic ferric sulphate was obtained some years ago from the firm of J. T. Baker and an analysis (33.61 per cent Fe_2O_3, 42.12 per cent SO_3, and by difference 24.27 per cent H_2O) was found to approach the composition of the basic salt $2Fe_2O_3.5SO_3.17H_2O$. It was extremely fine-grained and for that reason could not be definitely identified microscopically. The suspension of finely divided cupric oxide was prepared by adding a dilute solution of sodium hydroxide to a fairly concentrated warm solution of cupric sulphate, with constant stirring, until it became just alkaline. The greenish-blue precipitate first formed changed at this point to a brownish-black one which was cupric oxide as was evidenced by its X-ray diffraction pattern. The precipitate was washed by shaking it up with hot water and throwing it down by centrifuging. This was continued until the finely divided cupric oxide began to form a suspension which was no longer precipitated by ordinary centrifuging (approximately a relative centrifugal force of 1100 times gravity). The suspension prepared in this way was found by an analysis to be practically free from sodium.

From appropriate amounts of the materials described above mixtures of definite total composition were prepared which, on reaching equilibrium, furnished sufficient amounts of liquid and solid phases for their identification. The total amounts of the mixtures ranged from about 40 to about 100 grams. Each mixture was sealed in a Jena combustion tube, which it about two-thirds filled. These tubes were placed in an air thermostat at 50° in which the variation of temperature was limited to about ± 1°. The time the tubes were kept in the thermostat ranged from about one to about three years and during this time they were shaken up,almost every day to promote the establishment of equilibrium.

After the tubes were taken out of the thermostat they were quickly opened and the solid separated from the liquid phase by suction filtration through a dense Jena glass filter. A sample of the solid with adhering mother liquid was examined microscopically for control. The rest of the solid was washed with a mixture of water and alcohol and finally with alcohol or acetone. The air-dry solid was subjected to careful microscopical examination and X-ray analysis to establish the nature of the phase or phases present. Despite the extreme fineness of the precipitates representing the solid phases, it was in all cases possible to establish definitely their crystallinity and crystal individuality even when more than one solid phase was present in the precipitate.

The liquid, or a portion thereof, was weighed and analyzed. The following procedure was used: The copper was removed first by electrolysis of the solution, and weighed. The remaining solution, largely increased in volume due to washing of the copper precipitate, was partially evaporated and at the same time the iron which was reduced during electrolysis was re-oxidized by the addition of a few drops of "perhydrol" to the solution. A double precipitation of the iron with ammonia in the usual way followed and the iron on ignition was determined as oxide. In the combined filtrates the sulphate was finally determined, also gravimetrically, as barium sulphate. This method had been tried out with a mixture of standard solutions of copper and iron sulphates and was found in the absence of nitric acid to give accurate results. Water in all cases was taken by difference.

The Crystalline Phases

Geometrical and optical crystallographic descriptions of all of the compounds found in the portion of the quaternary system investigated have already been published.[1] In this paper the mode of occurrence of all these in the quaternary system will be described and X-ray powder diffraction patterns will be given for two of them, $Fe_2O_3.H_2O$ (goethite) and $3Fe_2O_3.4SO_3.9H_2O$, the patterns of the others having already been published.[2]

$Fe_2O_3.H_2O$ (Goethite).[2a] No single faceted crystals of goethite formed in the quaternary system at 50° (the only temperature at which experiments were carried out in the quaternary system), or in the ternary system, Fe_2O_3-SO_3-H_2O, at 50° or at any other temperature. Spherulites of goethite, single and in aggregates, were formed in one ternary solution at 50° and in other ternary solutions at higher temperatures. All of the goethite preparations formed in solutions containing all four components at 50° consisted of fibrous or optically amorphous aggregates. In all cases, however, their crystallinity and identity were established by the X-ray powder diffraction method. The apparatus used was one made by the General Electric Company in which the K_α radiation of molybdenum is used and the distance between sample and photographic film is eight inches. As a standard of comparison well-crystallized goethite from Pribram, Bohemia (Harvard Museum No. 80927), was utilized, of which the measured spacings of the diffraction lines and their estimated relative intensities are given in Table I.[3]

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[1] E. Posnjak and H. E. Merwin: The Hydrated Ferric Oxides, Am. J. Sci., **47**, 320 (1919); E. Posnjak and H. E. Merwin: The System, Fe_2O_3-SO_3-H_2O, J. Am. Chem. Soc., **44**, 1977 (1922); E. Posnjak and G. Tunell: The System, Cupric Oxide-Sulphur Trioxide-Water, Am. J. Sci., **18**, 12-23 (1929).

[2] Am. J. Sci., **18**, 12 (1929).

[2a] The usage of the term goethite in this paper is the same as that in earlier papers from this Laboratory; the term goethite is thus used as a synonym of α-$Fe_2O_3.H_2O$. It may be added that in this Laboratory the term lepidocrocite is used as a synonym of γ-$Fe_2O_3.H_2O$. These usages are consistent with those of most other authors. Unfortunately, however, by Willmann (Cbl. Min., **1921**, 673) and in "Gmelins Handbuch der anorganischen Chemie" (8. Aufl., Teil A, S. 147 (1929)) the term goethite has recently been applied to γ-$Fe_2O_3.H_2O$. For a clear statement of the history and present usages of the terms see "Handbuch der anorganischen Chemie" (Vierter Band, dritte Abteilung, zweiter Teil, B, Lieferung 1, S. B224, B225 (1930)) by R. Abegg, Fr. Auerbach, and I. Koppel. These authors use the terms goethite and lepidocrocite in the same senses in which they are used in the Geophysical Laboratory. Abegg, Auerbach, and Koppel give a good summary in tabular form of the geometrical, optical, and X-ray crystallographic properties, the densities, and some other physical properties of the dimorphic forms of $Fe_2O_3.H_2O$ (S. B226).

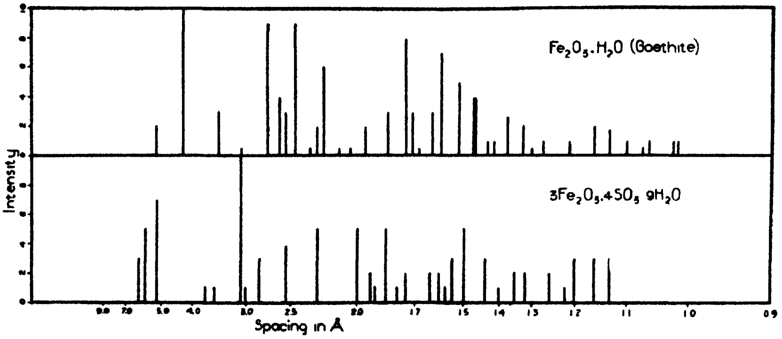

FIG. I

Diagrams of X-ray powder diffraction patterns of $Fe_2O_3.H_2O$ (goethite) and $3Fe_2O_3.4SO_3.9H_2O$. The relative intensities are visual estimates with ten representing the maximum in each case.

$3Fe_2O_3.4SO_3.9H_2O$. Faceted crystals of $3Fe_2O_3.4SO_3.9H_2O$ and aggregates of fine anhedral grains formed in ternary solutions of Fe_2O_3-SO_3-H_2O at 50°. In solutions containing all four components no faceted crystals formed but only fine-grained (crystalline) aggregates of anhedral, equant grains which were identified microscopically and by means of their X-ray powder diffraction pattern. Crystals of $3Fe_2O_3.4SO_3.9H_2O$[4] precipitated in a ternary solution of Fe_2O_3-SO_3-H_2O were used to obtain the standard X-ray spectrum of this substance. The measured spacings of the lines in the standard spectrum and their estimated relative intensities are given in Table I.

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[3] The diffraction pattern obtained from this specimen was identical with that obtained from one of goethite from El Paso County, Colorado, the analysis of which was No. 5 in Table I and the specific gravity No. 5 in Table VII of "The Hydrated Ferric Oxides" (Am. J. Sci., 47, 316 (1919)). Powder from the specimen from El Paso County, Colorado, was examined under the microscope by Merwin and by Tunell. No impurities were found. The powder consisted of brown, transparent to translucent grains some of which were perceptibly pleochroic between slightly different shades of brown. Grains lying approximately parallel to the perfect cleavage exhibited the characteristic green interference color already mentioned by Merwin and these also showed a biaxial optical figure.

[4] Identified optically. The optical properties of analyzed crystals formed in the system, Fe_2O_3-SO_3-H_2O, had been established previously by Posnjak and Merwin.

TABLE I

Planar Spacings and Estimated Relative Intensities of the X-ray Diffraction Lines of $Fe_2O_3.H_2O$ (Goethite) and $3Fe_2O_3.4SO_3.9H_2O$

$Fe_2O_3.H_2O$ (Goethite)		$3Fe_2O_3.4SO_3.9H_2O$	
Spacing	Intensity	Spacing	Intensity
5.1	2	6.0	3
4.24	10	5.7	5
3.42	3	5.15	7
3.07	0.5	3.69	1
2.72	9	3.54	1
2.61	4	3.10	10
2.52	3	3.00	1
2.475	9	2.84	3
2.325	0.5	2.56	4
2.275	2	2.27	5
2.220	6	1.99	5
2.110	0.5	1.935	2
2.040	0.5	1.890	1
1.940	2	1.840	5
1.820	3	1.780	1
1.732	8	1.745	2
1.704	3	1.631	2
1.675	0.5	1.595	2
1.615	3	1.570	1
1.578	7	1.545	3
1.520	5	1.503	5
1.470 (broad)	4	1.441	3
1.431	1	1.391	1
1.403	1	1.351	2
1.372	3	1.320	2
1.325	2	1.252	2
1.301	0.5	1.230	1
1.271	1	1.200	3
1.208	1	1.160	3
1.157	2	1.134	3
1.131	2	Further weak lines present	
1.100	1		
1.075	0.5		
1.057	1		
1.033	1		
1.018	1		
Further weak lines present			

CuO (Tenorite). No tenorite formed in our solutions containing all four components, and the precipitates which formed in the ternary system, $CuO-SO_3-H_2O$ (which is a part of the quaternary system), have already been described.[5]

$4CuO.SO_3.3H_2O$ (Brochantite). Minute lath-shaped single crystals of brochantite with positive elongation formed in one solution containing all four components.

$3CuO.SO_3.2H_2O$ (Antlerite). Minute lath-shaped single crystals of antlerite, some with negative, a few with positive elongation, were observed which formed in one solution containing all four components. These crystals were elongated parallel to β, like the crystals synthesized in the ternary system, $CuO-SO_3-H_2O$.

General Experimental Results

The isothermal-isobaric equilibrium relations in a quaternary system may be represented in an equilateral coordinate tetrahedron. The water corner of the tetrahedron, that is to say, the region in which the total composition is 93.5 per cent or more H_2O, 6.5 per cent or less Fe_2O_3, 6.5 per cent or less CuO, and 6.5 per cent or less SO_3, has been investigated at 50°C. and the results are presented in Table II. In order to be sure of the relations of the three-phase space curves inside the limited portion some points were also obtained just outside (that is, in more concentrated solutions), and these are

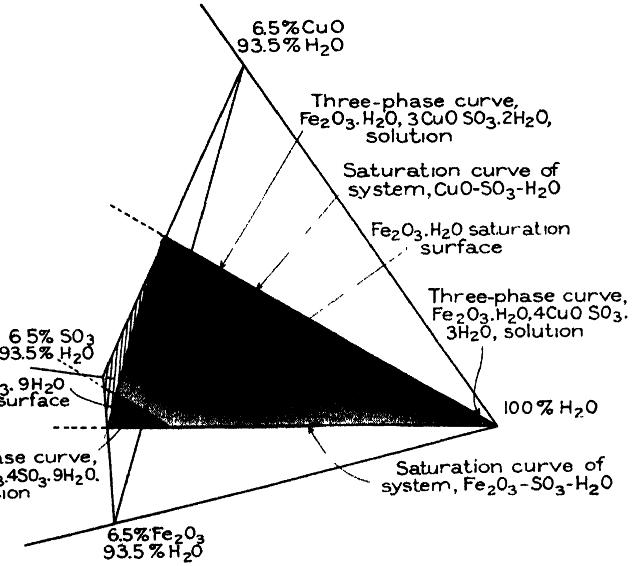
6.5%CuO
93.5%H₂O
Three-phase curve, Fe₂O₃.H₂O, 3CuO SO₃.2H₂O, solution
Saturation curve of system, CuO-SO₃-H₂O
Fe₂O₃.H₂O saturation surface
Three-phase curve, Fe₂O₃.H₂O,4CuO SO₃.3H₂O, solution
6.5% SO₃
93.5% H₂O
3Fe₂O₃.4SO₃.9H₂O saturation surface
100% H₂O
Three-phase curve, Fe₂O₃ H₂O,3Fe₂O₃.4SO₃.9H₂O. solution
Saturation curve of system, Fe₂O₃-SO₃-H₂O
6.5% Fe₂O₃
93.5% H₂O

FIG. 2

Perspective view of model of the isothermal-isobaric saturation surface in the portion of the system, $Fe_2O_3-CuO-SO_3-H_2O$, in which the total composition is 93.5 per cent or more H_2O, 6.5 per cent or less Fe_2O_3, 6.5 per cent or less CuO, and 6.5 per cent or less SO_3.

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[5] Am. J. Sci., 18, 14 (1929).

TABLE II

The Saturation Surface of the System, Ferric Oxide-Cupric Oxide-Sulphur Trioxide-Water, at 50° inside and just outside the Limited Portion of the Tetrahedron

Expt.	Liquid Phase				Solid Phases	Methods of Identification of Solid Phases[3]
	Fe_2O_3 %	CuO %	SO_3 %	H_2O[2] %		
8A	>0 <0.001	0.06	0.06	99.88	Fe_2O_3 H_2O[5] & $4CuO.SO_3.3H_2O$[4]	x o x o
9A	>0 <0.001	0.14	0.15	99.71	$Fe_2O_3.H_2O$[5] & $4CuO.SO_3.3H_2O$[7]	x o x
5A[1]	0.05	0.08	0.39	99.48	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
6A[1]	0.17	0.15	0.74	98.94	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
11A	>0 <0.001	0.61	0.64	98.75	$Fe_2O_3.H_2O$[5] & $4CuO.SO_3.3H_2O$	x o x
1A[1]	0.22	0.94	1.64	97.20	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[6]	x o x o
7A[1]	0.94	0.24	2.08	96.74	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
2A[1]	0.67	0.93	2.34	96.06	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
3A[1]	1.19	0.90	3.05	94.86	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[6]	x o x o
14A[1]	1.37	1.21	3.68	93.74	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
15A[1]	1.72	1.20	4.24	92.84	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
17A[1]	2.44	1.86	5.69	90.01	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
18A	>0 <0.001	5.01	5.22	89.77	$Fe_2O_3.H_2O$[5] & $3CuO.SO_3.2H_2O$[4]	x o x o

[1] The small amount of $3Fe_2O_3.4SO_3.9H_2O$ left in this experiment is probably due to the extreme slowness of the conversion of $3Fe_2O_3.4SO_3.9H_2O$ into $Fe_2O_3.H_2O$. The point therefore may be assumed to lie on the $Fe_2O_3.H_2O$ saturation surface. See discussion in text.

[2] H_2O by difference.

[3] Denotation of symbols: x, X-ray diffraction pattern; o, optical properties.

[4] Solid phase in faceted crystals.

[5] Solid phase in very fine-grained crystalline (fibrous) aggregates.

[6] Solid phase in very fine-grained crystalline aggregates (anhedral, equant grains).

[7] Solid phase not discernible under the microscope.

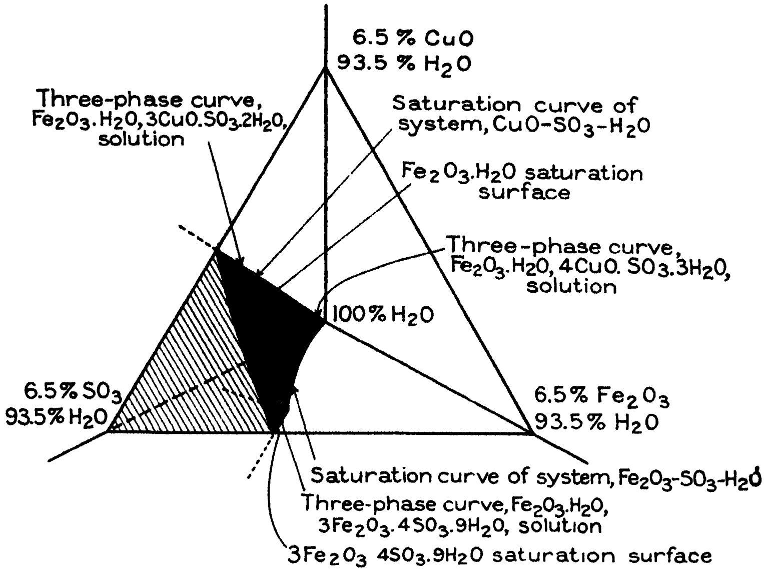
6.5 % CuO
93.5 % H2O
Three-phase curve, Fe2O3.H2O,3CuO.SO3.2H2O, solution
Saturation curve of system, CuO-SO3-H2O
Fe2O3.H2O saturation surface
Three-phase curve, Fe2O3.H2O, 4CuO. SO3.3H2O, solution
100% H2O
6.5% SO3
93.5% H2O
6.5% Fe2O3
93.5% H2O
Saturation curve of system, Fe2O3-SO3-H2O
Three-phase curve, Fe2O3.H2O, 3Fe2O3.4SO3.9H2O, solution
3Fe2O3 4SO3.9H2O saturation surface

Fig. 3

Perspective view of model of the isothermal-isobaric saturation surface in the portion of the system, Fe_2O_3-CuO-SO_3-H_2O, in which the total composition is 93.5 per cent or more H_2O, 6.5 per cent or less Fe_2O_3, 6.5 per cent or less CuO, and 6.5 per cent or less SO_3.

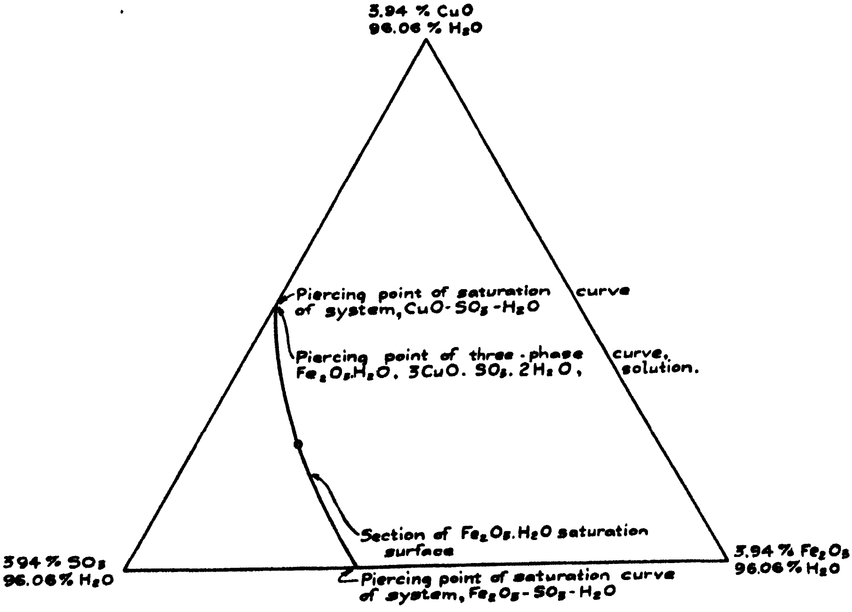
3.94 % CuO
96.06 % H2O
Piercing point of saturation curve of system, CuO-SO3-H2O
Piercing point of three-phase curve, Fe2O3.H2O, 3CuO. SO3. 2H2O, solution.
Section of Fe2O3.H2O saturation surface
3.94 % SO3
96.06% H2O
3.94 % Fe2O3
96.06 % H2O
Piercing point of saturation curve of system, Fe2O3-SO3-H2O

Fig. 4

Section through Fe_2O_3-CuO-SO_3-H_2O coordinate tetrahedron parallel to Fe_2O_3-CuO-SO_3 face (percentage of H_2O at all points in plane of section is 96.06).

also given in Table II. The data refer to mixtures at equilibrium except in cases explicitly noted in which the direction of a reaction was used to obtain information regarding the location of the three-phase curve, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution. A model of the portion of the tetrahedron and saturation surface has been prepared, and is illustrated in perspective in Figs. 2 and 3. A cross-section of the tetrahedron and saturation surface is given in Fig. 4. The concentrations are expressed numerically and graphically in weight per cent.

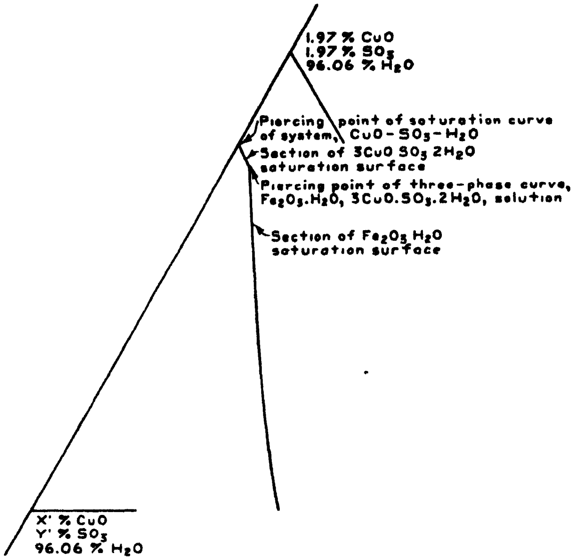
1.97 % CuO
1.97 % SO3
96.06 % H2O
Piercing point of saturation curve of system, CuO-SO3-H2O
Section of 3CuO SO3 2H2O saturation surface
Piercing point of three-phase curve, Fe2O3.H2O, 3CuO.SO3.2H2O, solution
Section of Fe2O3 H2O saturation surface
X' % CuO
Y' % SO3
96.06 % H2O

FIG. 5

Sketch showing relations which must exist very near the CuO-SO_3-H_2O face of the coordinate tetrahedron along trace of saturation surface on plane parallel to Fe_2O_3-CuO-SO_3 face (percentage of H_2O at all points in this plane is 96.06). Enormously enlarged as compared with Fig. 4.

The saturation surface of the quaternary system necessarily intersects the Fe_2O_3-SO_3-H_2O and CuO-SO_3-H_2O faces of the coordinate tetrahedron in the saturation curves of the respective ternary systems. Numerical values of the data for the saturation curve of the system, Fe_2O_3-SO_3-H_2O, have been given by Posnjak and Merwin and for the saturation curve of the system, CuO-SO_3-H_2O, by Posnjak and Tunell.[6] Some additional points have been determined in these systems. Six points on the saturation curves of the basic cupric sulphates are given in Table III. Also three points on the saturation curves of the normal cupric sulphates are given in Table III.[7] These three points are more accurate than point 81 of Table VI of "The System, Cupric

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[6] In the papers on the systems, Fe_2O_3-SO_3-H_2O and CuO-SO_3-H_2O, the results were expressed as isothermal-polybaric equilibria of crystal, liquid, and gas phases. As stated in the paper on the system, CuO-SO_3-H_2O, however, the pressure in the gas phase was greater than the vapor pressure of the solution by the pressure of the admixed air. It was also stated in that paper that any one of the diagrams presented would not differ more than the experimental error from the isothermal-isobaric diagram for the equilibria of crystal and liquid phases at the same temperature and the maximum pressure in any of the tubes. In the present paper the equilibria are treated as isothermal-isobaric equilibria of crystal and liquid phases: in the present work the pressures in all of the tubes were practically the vapor pressure of water plus the pressure of the admixed air at 50°C.

[7] Since publication of "The System, Cupric Oxide-Sulphur Trioxide-Water" by Posnjak and Tunell, there has appeared a paper entitled "The System: $CuSO_4$-H_2SO_4-H_2O" by H. D. Crockford and L. E. Warrick: J. Phys. Chem., **34**, 1064 (1930). These authors present data for the triple point, $CuO.SO_3.5H_2O$, $CuO.SO_3.3H_2O$, solution, at 40° and at 55°, and for the triple point, $CuO.SO_3.3H_2O$, $CuO.SO_3.H_2O$, solution, also at 40° and at 55°. Interpolation between their values of the SO_3 percentage at 40° and at 55° gives at 50° the SO_3 percentage 35.5 for the triple point, $CuO.SO_3.5H_2O$, $CuO.SO_3.3H_2O$, solution; this value lies within our brackets which are 34.46 and 37.58 per cent SO_3 (Table VI, Am. J. Sci., **18**, 33 (1929)). Interpolation between the values of the SO_3 percentage of Crockford and Warrick at 40° and at 55° gives at 50° the SO_3 percentage 44.5 for the triple point, $CuO.SO_3.3H_2O$, $CuO.SO_3.H_2O$, solution, which lies outside our brackets which are 38.50 and 43.04 per cent SO_3 (Table III of present paper). Moreover, interpolation between the less concentrated ends of the brackets of Crockford and Warrick for this triple point at 40° and at 55° gives a less concentrated end at 50° of 44.2 per cent SO_3. This conflicts with the more concentrated end of our brackets at 50°, 43.04 per cent SO_3. Plotting the analyses of the solutions and residues in experiments 8 (55°) and 9 (55°) of Crockford and Warrick and drawing the tie lines shows that apparently both $CuO.SO_3.3H_2O$ and $CuO.SO_3.H_2O$ were present in 8 (55°) and also in 9 (55°), provided that their analyses are accurate. It should be noted that they had no evidence except the analyses, as they did not examine the crystalline phases under the microscope. Similarly, plotting the analyses of the solutions and residues in experiments 8 (40°), 10 (40°), 11(40°), and 13 (40°) and drawing the tie lines shows that apparently again both $CuO.SO_3.3H_2O$ and $CuO.SO_3.H_2O$ were present in each case. The presence of two crystalline phases in more than one experiment at a given temperature is in contradiction to the phase rule and thus it seems that equilibrium in the solid phases was not attained in the experiments of Crockford and Warrick near the triple point, $CuO.SO_3.3H_2O$, $CuO.SO_3.H_2O$, solution, at 55° and at 40°. This is not surprising, as we have found that in a bottle which was kept in the thermostat at 50° much longer than the bottles of Crockford and Warrick, the conversion of the trihydrate into the monohydrate went on over a considerable period of days (even though the bottle was shaken frequently), as was proved by successive microscopic examinations of samples of the crystalline phases.

The general statement can be made that in phase rule studies in which the method of residues is used, the results can be accepted without optical examination only when the tie lines hit points representing known compounds very accurately. In cases in which the tie lines pass by the points representing known compounds or assumed compounds, microscopical studies (or in some cases X-ray studies or both) must be made in addition to chemical analyses to ascertain whether the discrepancies are due to the presence of more than one phase, to adsorption, or to solid solution.

When all of their data are plotted and the tie lines drawn it is evident that Crockford and Warrick are not justified in placing the triple points more closely than within a range of several per cent of SO_3 in many cases.

In passing it may be remarked that the designation of the part of the system, CuO-SO_3-H_2O, studied by Crockford and Warrick, as the system, $CuSO_4$-H_2SO_4-H_2O, is open to criticism since compositions on the line-segment connecting the points representing H_2O and $CuSO_4$ do not form a binary system, at least within the range from room temperature to 200°. Mixtures on part of the line-segment connecting the points representing water and the normal cupric sulphate (5-, 3-, or 1-hydrate depending upon the temperature) on reaching equilibrium consist of solutions in which the ratio of SO_3 to CuO is slightly greater than 1 to 1 (mols per mol) and a small amount of crystalline basic cupric sulphate; mixtures on the rest of this line-segment on reaching equilibrium consist of the same two phases plus crystalline normal cupric sulphate. In other words the normal cupric sulphates dissolve incongruently in water, at least from room temperature to 200°. The amount of basic cupric sulphate formed by hydrolysis of normal cupric sulphate in water, although small at 50°, is readily visible to the unaided eye and at higher temperatures it is substantial. Taking $CuSO_4$, H_2SO_4, and H_2O as the components of the ternary system, one must therefore make use of negative masses of one component, H_2SO_4, in order to express the compositions of some of the solid phases present. This is of course permissible, but the use of negative masses of components is probably best avoided if positive masses of the same number of other components will suffice. The compositions of all of the phases can be expressed in terms of CuO, SO_3, and H_2O with use only of positive masses.

TABLE III

Additional Points on the Saturation Curve of the System, Cupric Oxide-Sulphur Trioxide-Water, at 50°[1]

Expt.	Liquid Phase CuO %	SO$_3$ %	H$_2$O[3] %	Solid with Some Mother Liquid CuO %	SO$_3$ %	Solid Phase	Methods of Identification of Solid Phase[4]	Methods of Separation of Phases[8]
44	0.05	0.05	99.90	25.65	6.52	$4CuO.SO_3.3H_2O$	r o x[5]	f
45	0.13	0.13	99.74	25.92	6.78	$4CuO.SO_3.3H_2O$	r o[5]	f
48[2]	2.20	2.22	95.58			$4CuO.SO_3.3H_2O$ $3CuO.SO_3.2H_2O$	o[5] o[6]	f
35[2]	4.73	4.75	90.52			$4CuO.SO_3.3H_2O$ $3CuO.SO_3.2H_2O$	a o x[5] a o[6]	f
34[2]	5.93	5.96	88.11			$4CuO.SO_3.3H_2O$ $3CuO.SO_3.2H_2O$	a[5] a o[6]	f
36[2]	6.52	6.57	86.91			$4CuO.SO_3.3H_2O$ $3CuO.SO_3.2H_2O$	a x[5] a o x[6]	f
111	3.28	38.50	58.22			$CuO.SO_3.3H_2O$	o[7]	p
112	2.35	43.04	54.61			$CuO.SO_3.H_2O$	o[7]	p
113	1.54	45.40	53.06			$CuO.SO_3.H_2O$	o[7]	f

[1] Cf. Table VI of "The System, Cupric Oxide-Sulphur Trioxide-Water" (Am. J. Sci., 18, 33 (1929)).

[2] Equilibrium between the solid phases was not attained in this experiment. Very fine-grained crystalline (fibrous) aggregates of $4CuO.SO_3.3H_2O$ were partially converted into euhedral crystals of $3CuO.SO_3.2H_2O$. The solution lies on the $3CuO.SO_3.2H_2O$ side of the triple point.

[3] H_2O by difference.

[4] Denotation of symbols: o, optical properties; x, X-ray diffraction pattern; r, analysis of residue; a, analysis of air-dry solid.

[5] Solid phase in very fine-grained (crystalline) fibrous aggregates.

[6] Solid phase in separate, euhedral crystals.

[7] Coarsely crystalline.

[8] Denotation of symbols: f, filtration; p, removal of solution by means of pipette through glass extension tube containing cotton filter.

Oxide-Sulphur Trioxide-Water," which is therefore discarded as being slightly in error. Three additional points on the saturation curve of the system, Fe_2O_3-SO_3-H_2O, are given in Table IV and are discussed in the following paragraphs.

In the published experiments in each of the systems, Fe_2O_3-SO_3-H_2O and CuO-SO_3-H_2O, at 50° equilibrium in the solid phases was not completely established at points close to the triple point nearest the water corner of the triangle, a combination of unfavorable factors rendering the reactions exceedingly slow near each of these two triple points. The triple point, $4CuO.SO_3.3H_2O$, $3CuO.SO_3.2H_2O$, solution, at 50° in the system, CuO-SO_3-H_2O, was definitely limited, however, by experiments in which very fine-grained crystalline (fibrous) aggregates of $4CuO.SO_3.3H_2O$ were partially converted into separate, single crystals of $3CuO.SO_3.2H_2O$: by these experi-

TABLE IV

Additional Points on the Saturation Curve of the System, Ferric Oxide-Sulphur Trioxide-Water, at 50°[1]

Expt.	Liquid Phase Fe_2O_3 %	SO_3 %	H_2O[2] %	Solid Phases	Methods of Identification of Solid Phases[3]	Method of Separation of Phases[4]
139	0.01	0.10	99.89	$Fe_2O_3.H_2O$[5]	o a	f
97	1.95	2.94	95.11	$Fe_2O_3.H_2O$[6] & $3Fe_2O_3.4SO_3.9H_2O$[7]	o a a	f
62	2.54	3.57	93.89	$Fe_2O_3.H_2O$[6,8] & $3Fe_2O_3.4SO_3.9H_2O$[6]	o a o a	f

[1] Cf. Table IX of "The System, Fe_2O_3-SO_3-H_2O" (J. Am. Chem. Soc., **44**, 1991 (1922)).

[2] H_2O by difference.

[3] Denotation of symbols: o, optical properties; a, analysis of air-dry solid.

[4] Symbol f denotes filtration.

[5] Spherulites, single and in aggregates.

[6] Solid phase in very fine-grained crystalline aggregates.

[7] The $3Fe_2O_3.4SO_3.9H_2O$ left in this experiment is probably due to the extreme slowness of the conversion of $3Fe_2O_3.4SO_3.9H_2O$ into $Fe_2O_3.H_2O$. The point therefore may be assumed to lie on the $Fe_2O_3.H_2O$ saturation curve. See discussion in text.

[8] The small amount of $Fe_2O_3.H_2O$ in this preparation may have formed in the thermostat or possibly at room temperature before the tube was placed in the thermostat. If it formed at 50° the experiment determines the triple point, otherwise a point on the $3Fe_2O_3.4SO_3.9HO$ saturation curve.

ments it was proved to lie either at lower concentrations than CuO 1.65 per cent, SO_3 1.68 per cent, or at exactly these concentrations, the first possibility being the more probable one. Since publication of the paper on the system, CuO-SO_3-H_2O, additional experiments were made over a period of two years in the attempt to partially or completely convert very fine-grained crystalline (fibrous) aggregates of $3CuO.SO_3.2H_2O$ into separate, single crystals of $4CuO.SO_3.3H_2O$ at 50° but these did not result in narrowing down the interval published in that paper, because it was not possible to prove such conversion.[8] In an experiment with the quaternary system, Fe_2O_3-CuO-SO_3-H_2O, at 50° single euhedral crystals of $4CuO.SO_3.3H_2O$ were formed in a solution containing 0.06 per cent CuO,[9] a trace of Fe_2O_3 (less than 0.001 per cent), and 0.06 per cent SO_3, which was kept in the thermostat approximately three years. This experiment proves not only the existence of the $4CuO.SO_3.3H_2O$-solution field at this temperature, but also shows that the triple point, $4CuO.SO_3.3H_2O$, $3CuO.SO_3.2H_2O$, solution, in the ternary system, CuO-SO_3-H_2O, must lie at a sulphur trioxide concentration between (or at) 0.06 per cent and (or) 1.68 per cent.

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[8] At 100° this partial conversion of fine-grained crystalline (fibrous) $3CuO.SO_3.2H_2O$ into separate, single crystals of $4CuO.SO_3.3H_2O$ had already been accomplished, as well as the complete conversion of fine-grained, crystalline (fibrous) $4CuO.SO_3.3H_2O$ into separate, single crystals of $3CuO.SO_3.2H_2O$.

[9] This analysis was published in a footnote at the end of "The System, Cupric Oxide-Sulphur Trioxide-Water" (Am. J. Sci., **18**, 34 (1929)). The percentage of CuO was given there as 0.05. Calculated to the third place the figure is 0.055 so it should have been given as 0.06 according to the accepted convention.

The triple point, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, in the system, Fe_2O_3-SO_3-H_2O, at 50° is more difficult to establish accurately because no single, faceted crystals of $Fe_2O_3.H_2O$ have been formed in this system at 50° or at any other temperature. However, excellent round spherulites of $Fe_2O_3.H_2O$ (Preparation 139), single and in aggregates, $n = 2.04 \pm 0.01$, were formed at 50° in solution very near the water corner, containing 0.01 per cent Fe_2O_3, 0.10 per cent SO_3 (that is, in solution far away from the triple point, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution). These spherulites, although very small (the diameters of the single spherulites are about 0.003 millimeter), show the stationary black cross between crossed nicols and four anisotropic quadrants.[10] The elongation of the fibers is positive (determined with the gypsum plate of first order red). It is true that not only crystalline spherulites but also strained spheres of glass show such a cross. The small spheres of $Fe_2O_3.H_2O$ were formed in solution at 50°, however, and it cannot be assumed that each and every one is a strained sphere of amorphous material. Furthermore, as H. E. Merwin has pointed out,[11] there is no known explanation for their spherical shape except the hypothesis that they are spherulites the fibers of which grew radially. Therefore Merwin and the authors believe that these spheres of $Fe_2O_3.H_2O$ are spherulites, and that they constitute valid evidence of continued crystallization. Such crystallization is strong evidence, in addition to that already published, that $Fe_2O_3.H_2O$ has a stability field at 50° in the system, Fe_2O_3-SO_3-H_2O. Preparations of $Fe_2O_3.H_2O$ formed nearer the triple point are not spherulitic but are anisotropic, fibrous (crystalline). At high concentrations of ferric oxide and sulphur trioxide at 50° single, faceted crystals of $3Fe_2O_3.4SO_3.9H_2O$ were produced. Near the triple point $3Fe_2O_3.4SO_3.9H_2O$ precipitated in aggregates of minute anisotropic, anhedral grains. In all cases of conversion of one solid phase into the other, so far as is known, the conversion was of $3Fe_2O_3.4SO_3.9H_2O$ into $Fe_2O_3.H_2O$. The triple point probably lies at a sulphur trioxide concentration between (or at) 2.94 per cent and (or) 3.57 per cent.[12] This conclusion is based upon the following two experiments at 50°. In the first (97) the solid phase consisted about one-half of $Fe_2O_3.H_2O$ (as examined under the microscope and according to the following analysis of an air-dry sample, Fe_2O_3 65.41 per cent, SO_3 16.82 per cent, H_2O by difference 17.77 per cent) and the composition of the liquid was Fe_2O_3 1.95 per cent, SO_3 2.94 per cent after approximately three months reaction in the thermostat. In the second (62) the solid phase consisted principally of $3Fe_2O_3.4SO_3.9H_2O$ with some $Fe_2O_3.H_2O$ (as examined under the microscope and according to the following analysis of an air-dry sample, Fe_2O_3 56.65 per cent, SO_3 27.08 per cent, H_2O by difference 16.27 per cent) and the composition of the liquid was Fe_2O_3 2.54 per cent, SO_3 3.57 per cent after approximately three months reaction in the thermostat.

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[10] Observed by Tunell. Similar but larger spherulites of $Fe_2O_3.H_2O$ which formed at 110° and which made up parts of the solid phases in preparations 115 and 116 mentioned in Table VII of "The System, Fe_2O_3-SO_3-H_2O" (J. Am. Chem. Soc., **44**, 1988 (1922)), had been studied in detail by H. E. Merwin and described in that article (Pp. 1972, 1973).

[11] Oral communication to the authors.

[12] The triple point was placed tentatively at 2.30 per cent SO_3 in "The System, Fe_2O_3-SO_3-H_2O" (J. Am. Chem. Soc., **44**, 1991 (1922)); but it almost certainly lies at a slightly higher SO_3 concentration.

The complete 50° isotherm of the system, Fe_2O_3-SO_3-H_2O, is reproduced in Fig. 6, slightly modified in accordance with the foregoing text. The complete 50° isotherm of the system, CuO-SO_3-H_2O, is reproduced in Fig. 7, also slightly modified in accordance with the foregoing text.

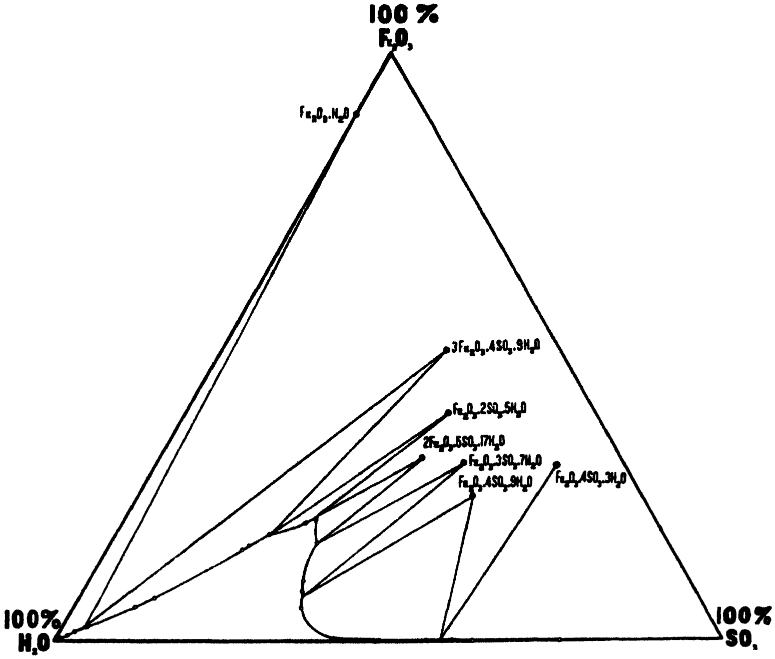

Fig. 6

The 50° isotherm of the system, Fe_2O_3-SO_3-H_2O. (Slightly modified after Posnjak and Merwin as explained in text.)

In the quaternary system at 50°C. the stable crystalline phases existing in contact with the various liquid phases having H_2O percentages above 93.5 are: $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, CuO, $4CuO.SO_3.3H_2O$, and $3CuO.SO_3.2H_2O$.

The three-phase curves lying in the saturation surface in the portion of the tetrahedron were limited as to location by the following experimental work. The three-phase curve, $Fe_2O_3.H_2O$, $4CuO.SO_3.3H_2O$, solution, was determined experimentally. The three-phase curve, $Fe_2O_3.H_2O$, $3CuO.SO_3.2H_2O$, solution, was sufficiently well oriented by the location of one point, as it is known to intersect the curve, $Fe_2O_3.H_2O$, $4CuO.SO_3.3H_2O$, solution, at an SO_3 concentration between (or at) 0.06 per cent and (or) 1.68 per cent and is almost a continuation of the latter curve. The position of the three-phase curve, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, was limited by experiments in which very fine-grained crystalline aggregates (anhedral grains) of $3Fe_2O_3.4SO_3.9H_2O$

were partially converted into crystalline (fibrous) aggregates of $Fe_2O_3.H_2O$. This conversion occurred in the $Fe_2O_3.H_2O$-solution field: it is thermodynamically impossible for it to occur in the $3Fe_2O_3.4SO_3.9H_2O$-solution field. The conversion therefore definitely limited the location of the three-phase curve. The extreme slowness of this conversion near the three-phase curve (complete equilibrium in the solid phases was not attained in these tubes after about three years' reaction in the thermostat) is due in part to the low solubility of both solid phases and probably also in part to a small difference between the chemical potentials. It is probable that the unstable continuation of the $3Fe_2O_3.4SO_3.9H_2O$ saturation surface in the $Fe_2O_3.H_2O$-solution field is very near the $Fe_2O_3.H_2O$ saturation surface in the vicinity of the three-phase curve (which is the intersection of the $3Fe_2O_3.4SO_3.9H_2O$ and $Fe_2O_3.H_2O$ saturation surfaces). Therefore, although in these tubes equilibrium was not completely established in the solid phases after about three years at constant temperature, no appreciable error is introduced by using the analyses of the solutions in them in the establishment of the saturation surface. The three-phase curves, $Fe_2O_3.H_2O$, CuO, solution; CuO, $4CuO.SO_3.3H_2O$, solution; and $4CuO.SO_3.3H_2O$, $3CuO.SO_3.2H_2O$, solution, are extremely short and on the scales of the plotted diagrams do not appear. These are all of the three-phase curves which occur in the portion of the quaternary system under consideration.

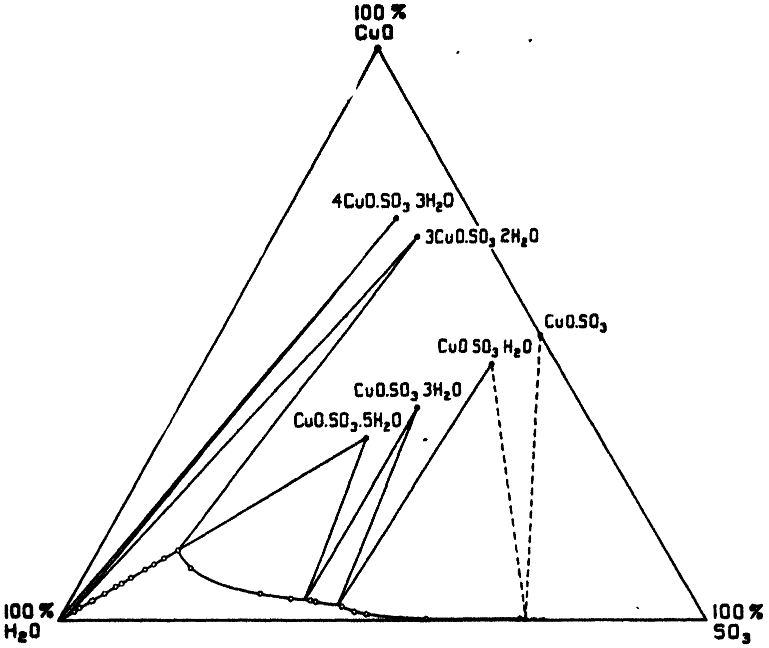

FIG. 7
The 50° isotherm of the system, CuO-SO_3-H_2O. (Slightly modified after Posnjak and Tunell as explained in text.)

General Properties of the Models for Quaternary Systems in which there is no Solid Solution[13]

The general properties of the isothermal-isobaric tetrahedral models for quaternary systems in which there is no solid solution are as follows. In the tetrahedron the percentages (by weight) of the four components of any arbitrary system are represented by the four normals to the faces of the tetrahedron from a particular point; this point may thus be said to represent the arbitrary system. The arbitrary systems, on reaching equilibrium, consist of one, two, three, or four phases, as shown by the locations of the points representing them in the subregions of the tetrahedron.

Arbitrary systems the total compositions of which are represented by points in the solution field form homogeneous solutions on reaching equilibrium.

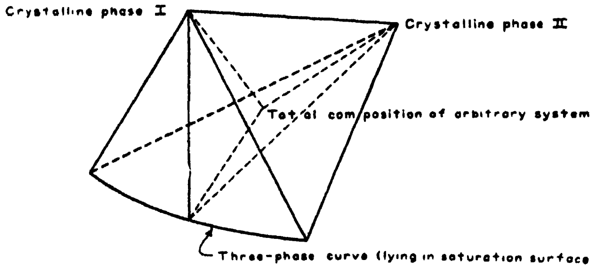
Crystalline phase I
Crystalline phase II
Total composition of arbitrary system
Three-phase curve (lying in saturation surface)

FIG. 8

Schematic illustration, in perspective, of general relations in a quaternary system in which there is no solid solution. The diagram shows the compositions of the crystalline phases and solution phase of an arbitrary system in a three-phase region. The weights of the three phases are to each other as the areas of the three subsidiary triangles opposite the points representing the compositions of the respective phases.

Arbitrary systems the total compositions of which are represented by points in any of the solids bounded by the saturation surface and a cone (noncircular) divide into two phases on reaching equilibrium, crystals the composition of which is represented by the apex and solution the composition of which is represented by the point in which the saturation surface is intersected by a straight line from the apex through the point representing the total composition of the arbitrary system. The weight of crystals is to the weight of solution as the segment of the line between the point representing the composition of the solution and the point representing the total composition of the arbitrary system is to the segment between the apex and the point representing the total composition of the arbitrary system.

Arbitrary systems the total compositions of which are represented by points in any of the solids bounded by two intersecting conical surfaces and two intersecting planes divide into three phases on reaching equilibrium, crystals of two kinds and solution. The compositions of the two kinds of crystals are represented by the endpoints of the segment between the two conical surfaces, of the intersection line of the two planes; the composition of the solution is represented by the point in which the curve common to the two conical surfaces (this curve lies in the saturation surface) is cut by a plane through the points representing the compositions of the two kinds of crystals and the point representing the total composition of the arbitrary system. The weights of the three phases are to each other as the areas of the three subsidiary triangles opposite the points representing the compositions of the respective phases. The construction of this paragraph is illustrated in Fig. 8.

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[13] The constructions of this section obviously also apply to parts of quaternary systems in which there is no solid solution although solid solutions may occur in other parts.

Lastly, arbitrary systems the total compositions of which are represented by points in any of the nonequilateral tetrahedra (within the equilateral coordinate tetrahedron) divide into four phases on reaching equilibrium, crystals of three kinds and solution, the compositions of which are represented by the vertices of the nonequilateral tetrahedron. The weights of the four phases are to each other as the volumes of the four subsidiary tetrahedra (together composing the nonequilateral tetrahedron) opposite the vertices of the nonequilateral tetrahedron representing the compositions of the respective phases.

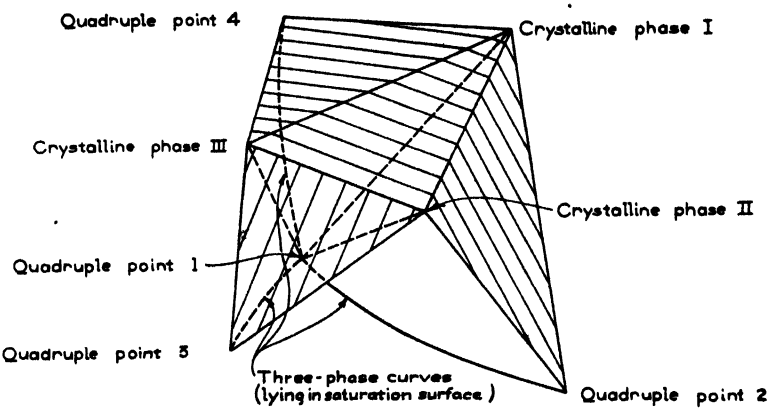

FIG. 9
Schematic illustration, in perspective, of general relations in a quaternary system in which there is no solid solution. The diagram shows the three three-phase curves (lying in the saturation surface) emanating from a quadruple point.

From each of the points representing the composition of a solution which is in equilibrium with three crystalline phases (quadruple points), that is to say, from the solution-vertex of each nonequilateral tetrahedron, there emanate three three-phase curves, points along which represent the compositions of solutions in equilibrium with two crystalline phases. Points in the areas of the saturation surface between the three-phase curves represent the compositions of solutions in equilibrium with one crystalline phase. The relations of this paragraph are illustrated in Fig. 9.

Description of the Three-Phase Curves in the Limited Portion of the System, Ferric Oxide-Cupric Oxide-Sulphur Trioxide-Water

The disposition of the six three-phase curves which occur in the portion of the system investigated is as follows. From the H_2O vertex of the coordinate tetrahedron there extends one three-phase curve, that of $Fe_2O_3.H_2O$, CuO, and solution, but it is extremely short and on the scale of the plotted model does not appear. From the end of this curve there emanate two others, that of CuO, $4CuO.SO_3.3H_2O$, and solution, which extends to the $CuO\text{-}SO_3\text{-}H_2O$ face of the coordinate tetrahedron and is thus too short to be visible if plotted on the same scale, and that of $Fe_2O_3.H_2O$, $4CuO.SO_3.3H_2O$, and solution, which extends almost parallel to the saturation curve of the system, $CuO\text{-}SO_3\text{-}H_2O$, and so near the latter that on the same scale the two curves cannot be shown separately. From the more concentrated end of the three-phase curve, $Fe_2O_3.H_2O$, $4CuO.SO_3.3H_2O$, solution, there emanate two more three-phase curves, that of $Fe_2O_3.H_2O$, $3CuO.SO_3.2H_2O$, and solution, which continues very near the saturation curve of the system, $CuO\text{-}SO_3\text{-}H_2O$, and that of $4CuO.SO_3.3H_2O$, $3CuO.SO_3.2H_2O$, and solution, which extends to the $CuO\text{-}SO_3\text{-}H_2O$ face of the coordinate tetrahedron, ending at the triple point, $4CuO.SO_3.3H_2O$, $3CuO.SO_3.2H_2O$, solution, of the system, $CuO\text{-}SO_3\text{-}H_2O$, and which is thus also too short to be visible if plotted on the same scale. The last three-phase curve is that of $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, and solution, which extends from the triple point, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, of the system, $Fe_2O_3\text{-}SO_3\text{-}H_2O$, to an endpoint not determined; the trend of the curve away from the triple point, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, of the system, $Fe_2O_3\text{-}SO_3\text{-}H_2O$, is such, however, that at successively higher CuO percentages the curve intersects planes parallel to the $Fe_2O_3\text{-}CuO\text{-}SO_3$ face of the coordinate tetrahedron in which the percentage of H_2O is successively lower (the planes referred to are those in any one of which the percentage of H_2O is a constant). The three-phase curve, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, passes through the plane in which the percentage of H_2O is 93.5 and out of the portion of the tetrahedron under consideration. The three-phase curves, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, and $Fe_2O_3.H_2O$, $3CuO.SO_3.2H_2O$, solution, thus do not intersect inside the limited portion of the quaternary system; they may or may not intersect outside.

Summary

The portion of the system, $Fe_2O_3\text{-}CuO\text{-}SO_3\text{-}H_2O$, in which the total composition is 93.5 per cent or more H_2O, 6.5 per cent or less Fe_2O_3, 6.5 per cent or less CuO, and 6.5 per cent or less SO_3, has been investigated at 50°C. with the purpose of applying the results to certain geologic problems.

The modes of occurrence, that is to say the crystallographic habits and states of aggregation, of the five crystalline phases, $Fe_2O_3.H_2O$ (goethite), $3Fe_2O_3.4SO_3.9H_2O$, CuO (tenorite), $4CuO.SO_3.3H_2O$ (brochantite), and $3CuO.SO_3.2H_2O$ (antlerite), encountered in this portion of the system are

described. No double salt has a stability field extending into the limited portion of the system.

Standard X-ray powder diffraction patterns are given for $Fe_2O_3.H_2O$ (goethite) and $3Fe_2O_3.4SO_3.9H_2O$.

The data for the saturation surface inside and just outside the limited portion of the system are presented in tabular form and the saturation surface is also illustrated by means of a model shown in perspective. The disposition of the six three-phase curves which lie completely or partly in the limited portion is described.

It is noteworthy from the geological standpoint that the $Fe_2O_3.H_2O$ saturation surface in the quaternary system extends from the saturation curve of $Fe_2O_3.H_2O$ in the system, Fe_2O_3-SO_3-H_2O, almost to the saturation curves of $4CuO.SO_3.3H_2O$ and $3CuO.SO_3.2H_2O$ in the system, CuO-SO_3-H_2O, the three-phase curves, $Fe_2O_3.H_2O$, $4CuO.SO_3.3H_2O$, solution, and $Fe_2O_3.H_2O$, $3CuO.SO_3.2H_2O$, solution, lying extremely close to the saturation curves of $4CuO.SO_3.3H_2O$ and $3CuO.SO_3.2H_2O$ in the system, CuO-SO_3-H_2O.

It is also of interest for its geological application that the three-phase curve, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, extending from the triple point, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, of the system, Fe_2O_3-SO_3-H_2O, at successively higher CuO percentages intersects planes parallel to the Fe_2O_3-CuO-SO_3 face of the coordinate tetrahedron in which the percentage of H_2O is successively lower (the planes referred to are those in any one of which the percentage of H_2O is a constant).

Geophysical Laboratory,
Carnegie Institution of Washington,
September, 1930.

THE SOLUBILITY OF POTASSIUM IODIDE IN WATER TO 240°

BY F. C. KRACEK

1. During the progress of another investigation it became desirable to know the course of the solubility curve of KI in water at temperatures above the normal boiling point of saturated solutions. Two series of data in this region are found in the literature, namely, by Tilden and Shenstone,[1] and Étard,[2] reaching to 175° and 213° respectively. There is considerable discrepancy between these two series; as will be seen later, the results of Étard are the more reliable, but the precision of the individual experiments is rather low.

Experimental

2. The solubility measurements were made by the synthetic method in Pyrex tubes. Known amounts of twice-recrystallized KI and distilled water were introduced into the tubes which were then sealed. The tubes were rotated in a stirred air bath which could be kept at any desired constant temperature; the presence or absence of crystals was determined by visual observation.[3] Particular attention was given to the determination of the disappearance of the last traces of crystals in the immediate proximity of the solubility point.

3. The bath was controlled by a five junction Cu-constantan couple actuating a commercial type of controller; the regulating junctions were bare, to minimize lag. The reading thermocouple was also Cu-constantan, enclosed in a small alundum mass, suspended immediately adjacent to the rotating solubility tube. This couple was calibrated with accepted standards, readings being made on a Wolff Feussner type potentiometer mounted in accordance with the usual practice. The control was reliable to better than ± 0.1°, and could be set and maintained at any desired temperature.

4. The solutions acquired a light brown tint due to slight hydrolytic decomposition of KI. This phenomenon is a familiar one, and can be eliminated by small additions of KOH. It was, however, thought better not to attempt to bring about decolorization by such additions, since to do so would alter the K-I ratio in the solutions.

The Results

5. The experimental data obtained in this work are recorded in Table I which gives all the necessary details. A comparison of these results with the older published determinations[4] is given in Fig. 1. The smooth curve is

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[1] Tilden and Shenstone: Proc. Roy. Soc., **35**, 345 (1883); Phil. Trans., **175**, 23 (1885).

[2] Étard: Ann. Chim. Phys., **2**, 503 (1894).

[3] F. C. Kracek: J. Phys. Chem., **35**, 417 (1931).

[4] For references see A. Seidell: "Solubilities of Inorganic and Organic Compounds" (1919); also Brönsted's section in Int. Crit. Tables **4**, 239; Scott and Frazier: J. Phys. Chem., **31**, 459 (1927); Scott and Durham: **34**, 1424 (1930).

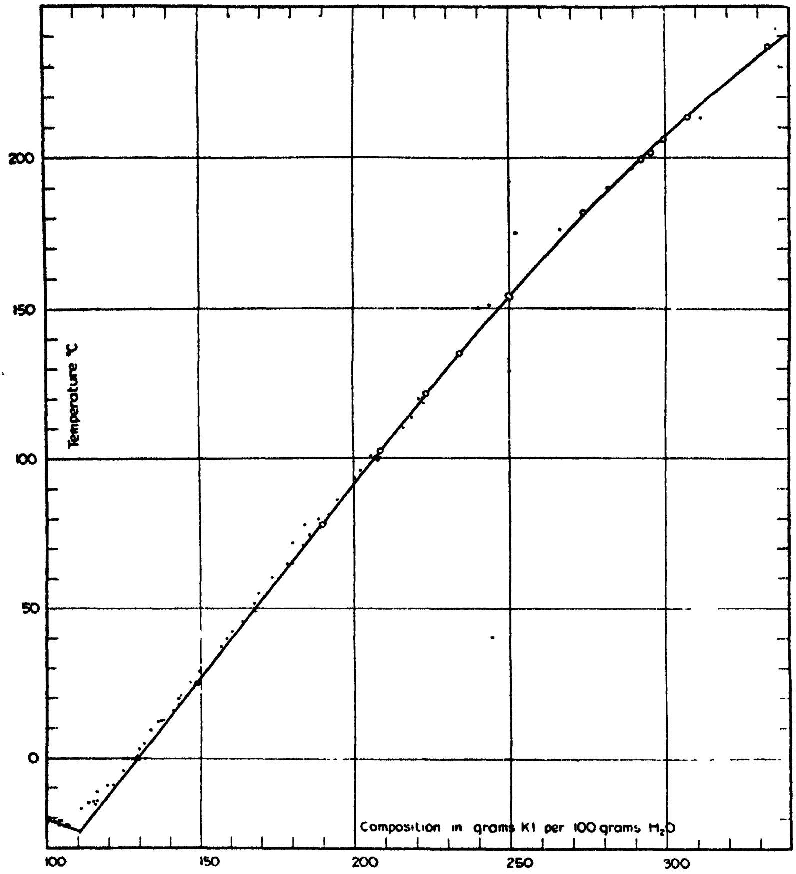

FIG. 1

Solubility of KI in water, in grams of KI per 100 grams of water. The small open circles from 150° upward are by Étard. The triangles at 0° and 25° are by Scott and co-workers, at 100° by Brönsted. The larger open circles are by Kracek. The small open circles at lower temperatures are taken at random from the literature.

passed thru Scott and Frazier's point at 25°; it also represents quite faithfully the results of Scott and Durham, the most recent published values for the region between 0° and 100°.

In the region of higher temperatures the curve falls generally among the points determined by Étard; the values by Tilden and Shenstone, however, are not even approximately correct.

This investigation is not properly concerned with values at low temperatures, but it may be permissible to point out that there appears to be a consistent deviation in some of the older results in the direction of unsaturation below 25°, and particularly in the determinations below 0°. If we accept Scott and Durham's and Scott and Frazier's determinations at 0° and 25°, both of which are almost directly on the curve as drawn, we must conclude

TABLE I

Determinations of solubility of KI in H_2O

Number	g KI	g H_2O	r_w*	r_m*	Percent KI weight	Percent KI mol	t°C
1	5.6805	2.9930	1.8979	0.20594	65.49	17.08	78.1
2	6.2164	2.9794	2.0865	.22641	67.60	18.46	102.4
3	5.7387	2.5686	2.2342	.24243	69.08	19.51	121.6
4	4.6109	1.9685	2.3423	.25416	70.08	20.265	134.9
5	5.4252	2.1685	2.5018	.27147	71.44	21.35	153.7
6	5.3133	2.1270	2.4980	.27106	71.41	21.33	154.3
7	5.3824	1.9658	2.7380	.29710	73.25	22.91	181.7
8	5.7625	1.9717	2.9226	.31713	74.51	24.08	199.3
9	7.9992	2.7074	2.9546	.32060	74.71	24.28	201.5
10	5.8592	1.9564	2.9949	.32498	74.97	24.53	206.0
11	6.1782	2.0104	3.0731	.33346	75.45	25.01	213.3
12	6.6479	1.9944	3.3333	.36170	76.92	26.56	236.4

* r_w = g KI per g of H_2O.
r_m = mols KI per mol of H_2O.

TABLE II

Solubility of KI in H_2O at even temperatures

t°C	g KI per 100 g H_2O	t°C	g KI per 100 g H_2O
0	129.1 ± 0.5	130	230.3 ± 0.5
10	136.8	140	238.5
20	144.5	150	246.7
30	152.2	160	255.0
40	159.9	170	263.7
50	167.6	180	272.9
60	175.3	190	282.6
70	183.0	200	292.9
80	190.8	210	303.4
90	198.6	220	314.3
100	206.4	230	326.0
110	214.3	240	338.4
120	222.3		

that these deviations are due to failure to obtain complete saturation, a very probable error in view of the high solubility of the salt.

Table II gives the values of the solubility of KI in H_2O at even temperatures, taken from the smooth curve of Fig. 1. The table thus represents the most probable values of the solubilities, arranged to facilitate interpolation at intermediate temperatures.

Geophysical Laboratory,
Carnegie Institution of Washington,
October, 1930.

THE STATISTICAL TREATMENT OF REACTION-VELOCITY DATA. II.

Least-Squares Treatment of the Unimolecular Expression: $Y = L\ (1 - e^{-Kt})$.*

BY LOWELL J. REED AND EMERY J. THERIAULT

Introduction

It has been shown in a previous paper[1] that the usual methods of calculating velocity constants are inadequate and that the least-squares procedures which have been proposed are inapplicable to unimolecular data.

In the present article a statistical treatment will be developed which permits of the ready derivation both of the experimental constants and of their precision values, proper allowance being made for constant errors. The discussion will be limited to the unimolecular expression

$$Y = L\ (1 - e^{-Kt})$$

and the applicability of the proposed method will be exemplified with reference to the data of Pennycuick[2] on the rate of inversion of sugar solutions. It will be shown that these observations conform very closely to the unimolecular type of equation. The data given by Daniels and Johnston[3] for the rate of decomposition of nitrogen pentoxide will also be briefly discussed.

1. Conditions affecting the Applicability of the Least-Squares Criterion

Before applying the least-squares criterion to a series of timed observations it will be necessary to establish the approximate validity of the following assumptions:

a. If all determinations had been made at any single time the absolute errors would have approximated a normal distribution.

b. The variation of this distribution would have been the same irrespective of the particular period of observation selected for the determinations.

c. The time, t, has been determined with a relatively high degree of precision so that the accidental errors in t are negligibly small in relation to the corresponding errors in Y.

d. Proper allowance has been made for constant errors.

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* From the Department of Biostatistics of the School of Hygiene and Public Health, of the Johns Hopkins University, Paper No. 145, and the Stream Pollution Investigation Laboratory, United States Public Health Service.

[1] The Statistical Treatment of Reaction-Velocity Data. I. A Critical Review of Current Methods of Computation. J. Phys. Chem., **35**, 673 (1931).

[2] Pennycuick, S. W. (1926): The Unimolecularity of the Inversion Process. J. Am. Chem. Soc., **48**, 6-19.

[3] Daniels, F., and Johnston, E. H. (1921): The Thermal Decomposition of Gaseous Nitrogen Pentoxide. A Monomolecular Reaction. J. Am. Chem. Soc., **43**, 53-71.

e. As a rule, the equation selected to represent a given process should either be in the linear form or else it should be possible to place it in the linear form without disturbing conditions (a) and (b) regarding the distribution of the errors.

The first assumption is generally valid in measurements based on readings of burettes, polarimeters, manometers, etc., if reference is made to the absolute error. As a rule, therefore, this condition will be fulfilled when the quantity directly observed is Y (or Z) in the equations

$$Y = L\,(1 - e^{-Kt}) \tag{1}$$

or,

$$Z = L\,e^{-Kt} \tag{2}$$

It is to be noted, however, that in investigations of supposedly unimolecular reactions, the selection of the quantity to be measured will generally be governed by considerations of analytical convenience. Conceivably (for instance, in potentiometric determinations) the quantity selected for measurement might be *ln* Z (or *ln* Y). In this case the equation representing the results would be

$$ln\,Z = ln\,L - Kt \tag{3}$$

In spectrophotometric work the quantity directly observed is a^{-Y} (or a^{-Z}), where "a" is a constant and, if the course of a reaction is followed by measuring a change in electrical resistance, the observed quantity may be $1/Y$ (or $1/Z$). The discussion which follows will be limited to the treatment of equation (1) and of the closely related equation (2). Equation (3) bears a formal resemblance to the Arrhenius expression

$$ln\,K_T = ln\,K_\infty - E/RT$$

and will be considered in a separate paper.

In particular cases the validity of the second assumption regarding the distribution of the errors may be tested out by the examination of pairs of observed values selected from different points along the curve. The assumption will be borne out when the absolute errors, as indicated by the difference between duplicate observations, do not seem to vary systematically with the time. Depending on the variable selected for measurement the percentage error will accordingly increase or decrease progressively with time.

The third assumption regarding the precision of the time measurements will be increasingly valid when slow reactions are considered.

The elimination of constant errors and the linearization of the equations will be considered in the discussion which immediately follows.

2. Allowance for Constant Errors

Let it be assumed that Y and t are the quantities obtained by direct observation and that these observations are supposedly represented by the unimolecular formula,

$$Y' = L'\,(1 - e^{-Kt'})$$

where the primes denote that the true values of Y, L and t are being considered. If the constant errors in either Y or t are known to be negligibly small in relation to the accidental (plus or minus) errors it may be permissible to use the above equation without modification. In general, however, it will be necessary to consider the possibility that either Y or t, or both, are affected by constant errors which approach or even exceed the magnitude of the accidental errors. To allow for such a contingency it may be assumed that, after correcting for known errors (lead or lag, etc.) the residual constant error in Y is q and that the corresponding error in t is r where q and r are small constant errors, either positive or negative. The formula which actually corresponds to the observations will then take the form

$$(Y-q) = L'\,[1-e^{-K(t-r)}]$$

where Y and t refer to the actual observations uncorrected for constant errors. From which

$$Y = L' + q - L'\,e^{-K(t-r)}$$

Factoring the second member of the above equation and simplifying the resulting expression

$$\begin{aligned} Y &= [L' + q]\,[1 - \left(\frac{L'}{L' + q}\right) e^{-K(t-r)}] \\ &= [L' + q]\,[1 - e^{Ks} \,.\, e^{-K(t-r)}] \\ &= [L' + q]\,[1 - e^{-K(t-r-s)}] \\ &= L\,[1 - e^{-K(t+w)}] \end{aligned} \qquad (5)$$

where,

$$\begin{aligned} \frac{L'}{L' + q} &= e^{Ks} \\ s &= \frac{1}{K}\,ln\left(\frac{L'}{L' + q}\right) \\ w &= -\,(r+s) \end{aligned} \qquad (6)$$

and,

$$L = L' + q$$

It follows that constant errors in the determination of Y and t may be accounted for by a shift, w, in the time-axis. It is to be borne in mind, therefore, that w in equation (5) refers not necessarily to a time error but rather to the resultant effect of all constant errors on the time. It is also to be noted that $L = L' + q$ corresponds to the limit which the observations are approaching when, of necessity, no correction can be applied for constant errors.

In experiments where the observed quantity is Z (the amount remaining) instead of Y (the amount decomposed) it will always be possible to express the results in terms of Y, provided that the approximate value of L is known. Thus,

$$Y = L - Z \qquad (7)$$

From the foregoing discussion it is apparent that any constant error introduced by this computation of Y will simply be absorbed in the term q. Equation (5) is therefore applicable to cases where the observed quantity is Z instead of Y.

Similarly it can readily be shown that equation (5) is applicable to results which are reported in terms of fractions (or percentages) of an experimentally determined value of L, without any presentation of the original observations from which the fractional values were derived.

3. Linearization of the Observational Equations

In general, the assumption that the observations Y and t are reasonably free from constant errors will seldom be satisfied in rate-of-reaction experiments. As a rule, therefore, the observations of a supposedly unimolecular process should be referred to the general expression

$$Y = L\,[1-e^{-K(t+w)}]$$

where, as already explained, w is a small quantity introduced to account for constant errors in the estimation of Y and t. For the purpose of reducing this expression to a linear form let it be assumed that an approximate value of K has first been obtained by any convenient method so that the most probable value of K is given by the relation

$$K = K' + h \tag{8}$$

where the trial value K′ is a true constant and h is a relatively small number, positive or negative, whose magnitude is to be determined. It will presently be shown that the assumed value of K′ need only be a rough approximation to the actual value of K, so that this assumption does not introduce any special difficulty. Similarly, let the constant w be represented by the relation

$$w = w' + i \tag{9}$$

where w′ is a first approximation to the value of w and i is a small constant whose magnitude is to be determined. It follows that

$$t + w = t + w' + i = t' + i \tag{10}$$

where $t' = t + w'$. By substitution in equation (5) we now obtain the equivalent expression

$$\begin{aligned} Y &= L\,[1-e^{-(K'+h)(t+i)}] \\ &= L\,[1-e^{-K't'}\,.\,e^{-Ki-ht'}] \end{aligned} \tag{11}$$

By definition, the exponent, $(-Ki-ht') = u$, is a small quantity. Using the relation

$$e^u = 1 + u$$

equation (11) may therefore be written

$$\begin{aligned} Y &= L\,[1-e^{-K't'}\,.\,(1-Ki-ht')] \\ &= L\,[1-e^{-K't'}] + Lh\,[t'e^{-K't'}] + LiK\,[e^{-K't'}] \end{aligned} \tag{12}$$

$$= af_1 + bf_2 + cf_3 \qquad (13)$$

where,

$$\begin{aligned} a &= L \\ b &= Lh \\ c &= LiK = Li\,(K'+h) \qquad (14) \\ f_1 &= 1-e^{-K't'} \\ f_2 &= t'e^{-K't'} \\ f_3 &= e^{-K't'} \end{aligned}$$

Equations (12) or (13) may be regarded as the linearized form of equation (5) where Y is a variable affected by accidental errors superimposed on a constant error; a, b, and c are statistical constants of unknown magnitude; and the time functions f_1, f_2 and f_3, are variables relatively free from accidental errors although not necessarily free from small constant errors. When h and i are each equal to zero, equation (12) evidently reduces to equation (1).

When no allowance is made for constant errors, that is, when the observations are referred to equation (1)

$$Y = L\,(1-e^{-Kt})$$

the linearized expression becomes

$$Y = L\,[1-e^{-K't}] + Lh\,[t'e^{-K't}] \qquad (15)$$

$$= af_1 + bf_2 \qquad (16)$$

where the significance of the symbols is denoted by equations (8) and (14). Equation (15) is obtainable from equation (12) by equating i to zero.

4. Tests for Unimolecularity

Considering the more general case represented by equation (5) or by the corresponding linearized expressions (12) or (13) and assuming that the conditions in regard to the nature and distribution of the errors have been satisfied, the various steps in testing the degree of conformity of a given process to an equation of the unimolecular type will be as follows:

a. Given a series of timed observations Y_1, Y_2, Y_3, etc., and the corresponding times t_1, t_2, t_3, etc., the constants L, K and w in equation (5) will first be determined by least-squares using a procedure which will presently be described.

b. The adjusted values of L, K and w will then be placed in equation (5) and, by assigning appropriate values to t, a series of calculated values, Y_1', Y_2', Y_3', etc., will be obtained which may be compared with the corresponding observations Y_1, Y_2, Y_3, etc.

c. The signs (+ or −) of the differences, $(Y_1 - Y_1')$, $(Y_2 - Y_2')$ etc., may then be examined for the presence of systematic divergencies between the observed and the calculated values. Provided that the observations actually conform to the unimolecular type of expression, a definite trend should not be observed if equation (5) has been used. If equation (1) has been used, the presence of a well-defined trend may indicate either a lack of conformity to the selected type of equation or else a necessity for making proper allowance for the presence of constant errors.

d. In the absence of a trend, the deviation, σ_y, defined by the relation

$$\sigma^2_y = \frac{\Sigma(Y-Y')^2}{n-3} \tag{17}$$

will then be computed. In equation (17) the number of observations, n, has been diminished by 3 to account for the 3 constants (L, K and w) which enter into the computation of Y′ by means of equation (5) (cf. Merriman, "Method of Least Squares," 1904, 8th edition revised, p. 82). When equation (1) is used the deviation σ_y will be given by the expression

$$\sigma^2_y = \frac{\Sigma(Y-Y')^2}{n-2} \tag{18}$$

where the number of observations, n, has been diminished by 2 to account for the 2 constants L and K.

By inspection of equations (17) and (18) it is apparent that, depending on the equation used, at least 3 or 4 observations must be made before any significance can be attached to the values of L and K found by least-squares.

The deviation, σ_y, is a measure of the agreement between the observed and calculated values. However, it should be emphasized that good agreement between observed and calculated values is not, of itself, a sufficient criterion of unimolecularity.

e. A comparison of σ_y with the standard deviation, σ, of the observations themselves, will indicate whether the agreement between the observed and calculated values is within the experimental error.

In favorable cases, the experimental error measured in terms of σ, may be found by the formula

$$\sigma^2 = \frac{\Sigma(Y'-Y'')^2}{2n} \tag{19}$$

where Y′ and Y″ are duplicate observations corresponding to any period of observation. Alternatively, the standard deviation may be found by making a large number of parallel observations at any single point on the curve.

In less favorable cases, it may be either impossible or inconvenient to conduct tests in duplicate or to obtain duplicate readings. Under these conditions it may, nevertheless, be possible to estimate the order of magnitude of σ by a consideration of known errors inherent to the analytical determination of Y.

f. Using σ_y, the deviations of L, K and w will then be computed by formulae which will shortly be derived. From the magnitude of these deviations definite conclusions may be drawn concerning the degree of confidence which can be placed on the agreement between the observed and calculated values of Y.

It will be noted that the above test for unimolecularity depends on the magnitude of the deviations of the constants K, L and w and on the precision measure, σ, of the observations themselves. On this basis K is obtained not as a series of values but as a single, weighted constant; L need not be determined experimentally but appears in the computation as the limiting value which the observations are actually tending to approach; and w is the resultant constant error in L and t. The procedure differs materially, therefore, from the usual criterion based on the possibility of deriving a consistent series of K values using an experimentally determined value of L and disregarding constant errors.

Apart from statistical considerations, it is obvious that the adoption of this method of computation should be advantageous whenever the experimental determination of L is difficult or uncertain (for example, in rate-of-inversion experiments) or in cases where a constant error is necessarily introduced in the measurement of the time (cf. Daniels and Johnston, 1921, p. 56). In such cases the added arithmetical labor may well be compensated for by the avoidance of experimental difficulties.

5. Derivation of the Normal Equations

As already shown (cf. Part I), the derivation of numerical values for the constants L and K from two observational equations of the type

$$Y = L\,(1-e^{-Kt}) = af_1 + bf_2$$

offers no difficulty. Similarly, the derivation of the constants L, K and w (or a, b, and c) from three equations of the type

$$Y = L\,[1-e^{-K(t+w)}] = af_1 + bf_2 + cf_3$$

could readily be accomplished. However, when the number of observational equations exceeds the number of unknown quantities (L, K and w in the above equation) the solution of the equations by the usual algebraic procedures becomes indeterminate. In such cases the most probable values of the unknown constants may nevertheless be obtained by the application of the least-squares criterion, namely, that the values of L, K and w (or the closely related quantities, a, b and c) are to be selected in such a manner that the sum, R, of the squares of the differences between the observed and calculated quantities shall be a minimum.

For equation (5) the difference between an observed and a calculated quantity is evidently

$$r = Y - af_1 - bf_2 - cf_3$$

and the sum, R, of the squares of the residual errors is

$$R = \Sigma\,(Y - af_1 - bf_2 - cf_3)^2$$

By definition, the most probable values of the constants a, b, and c, (corresponding to L, K and w) will be obtained when R is a minimum. From the calculus, the equations defining this condition are,

$$\frac{\delta R}{\delta a} = \Sigma f_1 Y - a\Sigma f_1^2 - b\Sigma f_1 f_2 - c\Sigma f_1 f_3 = 0 \qquad (20)$$

$$\frac{\delta R}{\delta b} = \Sigma f_2 Y - a\Sigma f_1 f_2 - b\Sigma f_2^2 - c\Sigma f_2 f_3 = 0 \qquad (21)$$

$$\frac{\delta R}{\delta c} = \Sigma f_3 Y - a\Sigma f_1 f_3 - b\Sigma f_2 f_3 - c\Sigma f_3^2 = 0 \qquad (22)$$

The solution of equations (20), (21) and (22) by the usual algebraic processes (cf. Woods and Bailey, "A Course in Mathematics," Vol. I, p. 2) gives:

$$a = \frac{[(\Sigma f_2 f_3)^2 - \Sigma f_2^2.\Sigma f_3^2]\Sigma f_1 Y + [\Sigma f_1 f_2.\Sigma f_3^2 - \Sigma f_1 f_3.\Sigma f_2 f_3]\Sigma f_2 Y + [\Sigma f_2^2.\Sigma f_1 f_3 - \Sigma f_1 f_2 \Sigma f_2 f_3]\Sigma f_3 Y}{\Sigma f_1^2[(\Sigma f_2 f_3)^2 - \Sigma f_2^2.\Sigma f_3^2] + \Sigma f_1 f_2[\Sigma f_1 f_2.\Sigma f_3^2 - \Sigma f_1 f_3.\Sigma f_2 f_3] + \Sigma f_1 f_3[\Sigma f_2^2.\Sigma f_1 f_3 - \Sigma f_1 f_2.\Sigma f_2 f_3]} \quad (23)$$

$$b = \frac{[\Sigma f_1 f_2.\Sigma f_3^2 - \Sigma f_1 f_3.\Sigma f_2 f_3]\Sigma f_1 Y + [(\Sigma f_1 f_3)^2 - \Sigma f_1^2.\Sigma f_3^2]\Sigma f_2 Y + [\Sigma f_1^2.\Sigma f_2 f_3 - \Sigma f_1 f_2.\Sigma f_1 f_3]\Sigma f_3 Y}{\Sigma f_1^2[(\Sigma f_2 f_3)^2 - \Sigma f_2^2.\Sigma f_3^2] + \Sigma f_1 f_2[\Sigma f_1 f_2.\Sigma f_3^2 - \Sigma f_1 f_3.\Sigma f_2 f_3] + \Sigma f_1 f_3[\Sigma f_2^2.\Sigma f_1 f_3 - \Sigma f_1 f_2.\Sigma f_2 f_3]} \quad (24)$$

$$c = \frac{[\Sigma f_2^2.\Sigma f_1 f_3 - \Sigma f_1 f_2.\Sigma f_2 f_3]\Sigma f_1 Y + [\Sigma f_1^2.\Sigma f_2 f_3 - \Sigma f_1 f_2.\Sigma f_1 f_3]\Sigma f_2 Y + [(\Sigma f_1 f_2)^2 - \Sigma f_1^2.\Sigma f_2^2]\Sigma f_3 Y}{\Sigma f_1^2[(\Sigma f_2 f_3)^2 - \Sigma f_2^2.\Sigma f_3^2] + \Sigma f_1 f_2[\Sigma f_1 f_2.\Sigma f_3^2 - \Sigma f_1 f_3.\Sigma f_2 f_3] + \Sigma f_1 f_3[\Sigma f_2^2.\Sigma f_1 f_3 - \Sigma f_1 f_2.\Sigma f_2 f_3]} \quad (25)$$

Use will presently be made of some of the coefficients in the above equations in deriving the respective weights of the constants a, b and c. These equations could also be used to determine the most probable values of a, b and c, although the arithmetical work will be shortened if the solution of a, b and c is made to depend directly on equations (20), (21) and (22), after the insertion in these equations of numerical values for the various sums;

$$\begin{array}{lll} \Sigma f_1 Y & \Sigma f_1^2 & \Sigma f_1 f_2 \\ \Sigma f_2 Y & \Sigma f_2^2 & \Sigma f_1 f_3 \\ \Sigma f_3 Y & \Sigma f_3^2 & \Sigma f_2 f_3 \end{array} \qquad (26)$$

6. Derivation of L, K and W

In illustration of the computations use will be made of the data given by Pennycuick (1916; p. 9, his Table II) for the rate of inversion of sugar solutions. Using equation (5) it will be assumed, for simplicity, that w′ is zero, so that $w = w' + i = i$. For convenience of computation the function $e^{-k't'}$ will be placed in the equivalent form $10^{-k't'}$ where

$$k' = 0.4342945\ K'$$

Using rounded numbers, the trial value of 0.001600 will be selected for k′ corresponding to a value of

$$(2.302585)\ (0.001600) = 0.0036841$$

for K′. Within wide limits, the exact numerical value of K′ is without significant influence on the final results.

In Table No. 1, the values of t′ are those given by Pennycuick (1926; p. 9). The values for Y (the sucrose remaining at the time t) were found by deduct-

TABLE I

Computations: Data of Pennycuick (1926, p. 9, His Table II)
($k' = 0.001600$; $w' = 0$)

$t' = t$	Y	$k't'$	$f_3 = 10^{-k't'}$	f_3^2	f_3Y	$f_2 = tf_3$	$f_2Y = t.f_3Y$	$f_2^2 = t^2.f_3^2$	$f_2f_3 = t.f_3^2$
5.97	2.0	0.009552	0.978246	0.956965	1.95649	5.84013	11.68	34.11	5.7131
9.82	3.5	.015712	.964468	.930199	3.37564	9.47108	33.15	89.70	9.1346
21.77	7.4	.034832	.922928	.851796	6.82967	20.09214	148.68	403.69	18.5436
29.80	10.2	.047680	.896025	.802861	9.13946	26.70155	272.36	712.97	23.9253
44.47	14.9	.071152	.848883	.720602	12.64836	37.74983	562.47	1425.05	32.0452
59.60	19.7	.095360	.802860	.644584	15.81634	47.85046	942.65	2289.67	38.4172
79.60	25.4	.127360	.745830	.556262	18.94408	59.36807	1507.95	3524.57	44.2785
93.18	29.0	.149088	.709434	.503297	20.57359	66.10506	1917.05	4369.88	46.8972
119.6	35.5	.191360	.643636	.414267	22.84908	76.97887	2732.75	5925.75	49.5464
142.9	40.9	.228640	.590691	.348916	24.15926	84.40974	3452.36	7125.00	49.8601
179.7	48.4	.287520	.515798	.266048	24.96462	92.68890	4486.14	8591.23	47.8087
239.8	58.9	.383680	.413352	.170860	24.34643	99.12181	5838.27	9825.13	40.9722
299.8	67.2	.479680	.331375	.109809	22.26840	99.34622	6676.07	9869.67	32.9209
359.7	73.9	.575520	.265754	.070625	19.63922	95.59171	7064.23	9137.78	25.4039
522.9	85.9	.836640	.145667	.021219	12.51280	76.16927	6542.94	5801.76	11.0953
589.4	88.9	.943040	.114015	.012999	10.13593	67.20044	5974.12	4515.90	7.6619
639.8	90.0	1.023680	.094694	.008967	8.60768	60.58522	5507.20	3670.57	5.7370
Sums	702.6	—	9.983656	7.390276	258.76705	1025.27050	53670.07	77312.43	489.9611

ing the percentage values for Z given by Pennycuick from 100. As many places of significant figures were retained as appeared necessary to provide about seven significant figures in the sums given at the bottom of Table I.

The computations in Table I will therefore furnish all of the sums listed under (26) with the exception of Σf_1Y, Σf_1^2, Σf_1f_2 and Σf_1f_3. Using the data given in Table No. 1, these sums may conveniently be obtained as follows:

$$\begin{aligned}
\Sigma f_1Y &= \Sigma Y - \Sigma f_3Y &&= 443.833\\
\Sigma f_1^2 &= n + \Sigma f_3^2 - 2\Sigma f_3 &&= 4.42296\\
\Sigma f_1f_2 &= \Sigma f_2 - \Sigma f_2f_3 &&= 535.309\\
\Sigma f_1f_3 &= \Sigma f_3 - \Sigma f_3^2 &&= 2.59338
\end{aligned}$$

Retaining only 6 places of significant figures and substituting in the normal equations (20), (21) and (22), the following numerical expressions are then obtained:

$$\begin{aligned}
\text{I}\quad & 443.833 - 4.42296\,a - 535.309\,b - 2.59338\,c = 0\\
\text{II}\quad & 53670.1 - 535.309\,a - 77312.4\,b - 489.961\,c = 0\\
\text{III}\quad & 258.767 - 2.59338\,a - 489.961\,b - 7.39028\,c = 0
\end{aligned}$$

These equations may now be solved by any of the usual algebraic methods. If a calculating machine is available the following procedure may be found convenient. Equations I, II and III are first divided, in turn, by the coefficients of c to obtain the 3 equations:

$$\text{IV}\quad 171.141 - 1.70548\,a - 206.414\,b - c = 0$$

$$\text{V}\quad 109.539 - 1.09255\,a - 157.793\,b - c = 0$$

$$\text{VI}\quad 35.015 - 0.35092\,a - 66.298\,b - c = 0$$

Equation VI is then subtracted from equations IV and V, thereby eliminating c, with the result,

$$\text{VII}\quad 136.126 - 1.35456\,a - 140.116\,b = 0$$

$$\text{VIII}\quad 74.524 - 0.74163\,a - 91.495\,b = 0$$

Equations VII and VIII are next divided by the coefficients of b to obtain

$$\text{IX}\quad 0.971524 - 0.0096674\,a - b = 0$$

$$\text{X}\quad 0.814514 - 0.0081057\,a - b = 0$$

On substracting X from IX the term b is eliminated, giving

$$\text{XI}\quad 0.157010 - 0.0015617\,a = 0$$

From which

$$a = 100.538$$

By substituting this value of a in IX

$$b = -0.000417$$

and by substitution in IV

$$c = -0.239$$

The arithmetical work may be checked by inserting the numerical values of a, b and c in III and balancing the equation.

Using (14), it follows that.

$$\begin{array}{lcccl} L & = & a & = & 100.538 \\ h & = & b/L & = & -0.0000041 \\ K' & = & 2.302585\,k' & = & 0.0036841 \\ K & = & K' + h & = & 0.0036800 \\ k & = & 0.4342945\,K & = & 0.0015982 \\ w & = & w' + i = i & = & \frac{c}{ak} = -\frac{0.239}{0.369980} = -0.646 \end{array}$$

7. Derivation of the Standard Deviation, σ_y

The adjusted values of L, k and w may now be substituted in equation (5) to obtain the series of calculated values given under the heading Y′ in Table II. By inspection, it is apparent that the agreement between the observed and the calculated values is excellent. For this series of observations the standard deviation is

$$\sigma_y = \sqrt{\frac{0.1684}{17-3}} = \sqrt{0.0120} = 0.11$$

corresponding to a probable error of (0.6745) (0.11) = 0.07 per cent. The agreement would not be appreciably altered if the calculation were to be repeated using the trial values k′ = 0.015982 and w′ = − 0.646.

The procedure exemplified in the foregoing pages has also been applied to another series of observations given by Pennycuick (1926, p. 8; his Table I). For these observations the adjusted values of k, L and w are 0.0006004, 100.275 and −0.268 respectively. As shown in Table IIa (17 observations) the agreement between the observed values and the values calculated by equation (5) is good although the general agreement is obviously affected by the presence of one discordant result. When all observations are considered, the value of σ_y is

$$\sigma_y = \sqrt{\frac{2.0809}{17-3}} = 0.39$$

Excluding the discordant observation, the adjusted values of k, L and w become, 100.317, −2.15 and 0.0006010, respectively. A recalculation of the standard deviation on this basis (Table IIa; 16 observations) gives

$$\sigma_y = \sqrt{\frac{0.1642}{16-3}} = 0.11$$

The agreement between the observed and calculated values (Y and Y″) is excellent.

In the absence of data on which a calculation of the deviation, σ, of the observations themselves can be based, it is perhaps safe to assume with Scatchard (1926) that the precision attainable in such measurements is in the neighborhood of 0.2 to 0.5 per cent. If so, it must be concluded that Pennycuick's data conform to the unimolecular type of expression within allowable limits of experimental error. In this sense it appears unnecessary to assume a progressive change of environment in these rate-of-inversion experiments. (Progressive increase in H-ion activity, etc.) However, to confirm this conclusion it will be necessary to obtain a measure of the precision of the constants which were used in deriving the calculated values.

TABLE II

Computation of σ_y for the Data of Pennycuick (1926, p. 9)
$k' = 0.0015982$; $w' = -0.646$; $L = 100.538$)

t	$t' = t + w$	$k't'$	$f_3 = 10^{-K't'}$	$f_1 = 1 - f_3$	Y observed	$Y' = Lf_1$ Calculated	$d = Y - Y'$	d^2
5.97	5 324	0.008509	0 980598	0.019402	2.0	1 95	0.05	0.0025
9.82	9 174	.014662	.966803	.033197	3 5	3 34	.16	.0256
21.77	21.124	033760	.925210	.074790	7 4	7.52	− .12	.0144
29.80	29.154	.046594	.898268	.101732	10.2	10.23	− .03	.0009
44.47	43.824	.070040	.851060	.148940	14.9	14.97	− .07	.0049
59.60	58.954	.094220	.804970	.195030	19 7	19.61	.09	.0081
79.60	78.954	.126184	747853	.252147	25.4	25 35	.05	.0025
93.18	92.534	.147888	.711397	288603	29.0	29.02	− .02	.0004
119.6	118.954	.190112	.645488	.354512	35.5	35.64	− .14	.0196
142.9	142.254	.227350	.592448	.407552	40.9	40.97	− .07	.0049
179.7	179.054	.286164	.517412	.482588	48.4	48.52	− .12	.0144
239.8	239.154	.382216	414748	.585252	58.9	58.84	.06	.0036
299.8	299.154	.478108	.332577	.667423	67.2	67 10	.10	.0100
359.7	359.054	.573840	.266784	.733216	73.9	73.72	.18	.0324
522.9	522.254	.834666	.146330	.853670	85.9	85.83	.07	.0049
589.4	588.754	.940947	.114565	.885435	88.9	89.02	− .12	.0144
639.8	639.154	1.021496	.095171	.904829	90.9	90.97	− .07	.0049
							$\Sigma d^2 =$	0.1684

TABLE IIa

Computation of σ_y for the Data of Pennycuick (1926, p. 8)

t	17 observations				16 observations			
	Y Observed	Y′ calculated[1]	d = Y−Y′	d²	Y Observed	Y″ Calculated[2]	d = Y−Y″	d²
19.80	2.5	2.35	0.15	0.0225	2.5	2.42	0.08	0.0064
39.71	5.0	5.00	.00	.0000	5.0	5.08	− .08	.0064
59.35	7.6	7.56	.04	.0016	7.6	7.63	− .03	.0009
63.01	8.0	8.02	− .02	.0004	8.0	8.10	− .10	.0100
77.50	10.0	9.85	.15	.0225	10.0	9.93	.07	.0049
101.41	13.0	12.79	.21	.0441	13.0	12.88	.12	.0144
181.61	22.0	21.97	.03	.0009	22.0	22.06	− .06	.0036
226.30	26.6	26.67	− .07	.0049	26.6	26.75	− .15	.0225
299.01	34.0	33.71	.29	.0841	34.0	33.80	.20	.0400
371.35	38.7	40.04	−1.34	1.7956	—	—	—	—
490.20	49.3	49.17	.13	.0169	49.3	49.26	.04	.0016
608.70	57.0	56.89	.11	.0121	57.0	56.98	.02	.0004
811.64	67.6	67.50	.10	.0100	67.6	67.59	.01	.0001
1100.60	78.2	78.30	− .10	.0100	78.2	78.38	− .18	.0324
1152.50	80.0	79.82	.18	.0324	80.0	79.90	.10	.0100
1486.40	87.4	87.38	.02	.0004	87.4	87.45	− .05	.0025
2696.40	98.0	97.85	.15	.0225	98.0	97.91	.09	.0081
			Σd^2 =	2.0809			Σd^2 =	0.1642

[1] Basis of L = 100.275; w′ = −2.68; k′ = 0.0006004.
[2] Basis of L = 100.317; w′ = −2.15; k′ = 0.0006010.

8. Derivation of the Weights and Standard Deviations of L, K, and w

Denoting the denominator common to equations (23), (24) and (25) by the symbol D_{abc}, it may readily be shown (cf. Merriman, "Method of Least-Squares," 1904, 8th edition revised, pp. 82-85, 195-198 or Mellor, "Higher Mathematics for Students of Chemistry and Physics," 1913, p. 559) that the weights of a, b and c are given by the expressions:

$$W_a = \frac{D_{abc}}{(\Sigma f_2 f_3)^2 - \Sigma f_2^2 . \Sigma f_3^2} \tag{27}$$

$$W_b = \frac{D_{abc}}{(\Sigma f_1 f_3)^2 - \Sigma f_1^2 . \Sigma f_3^2} \tag{28}$$

$$W_c = \frac{D_{abc}}{(\Sigma f_1 f_2)^2 - \Sigma f_1^2 . \Sigma f_2^2} \tag{29}$$

Given the weights of a, b and c, the deviations of these quantities are found by the formulae

$$\sigma_a = \frac{\sigma_y}{\sqrt{W_a}}; \quad \sigma_b = \frac{\sigma_y}{\sqrt{W_b}}; \quad \sigma_c = \frac{\sigma_y}{\sqrt{W_c}}$$

(cf. Mellor, p. 511). The calculations in question are exemplified in Table No. 3.

In deriving the deviation σ_K of K it may be considered that $\sigma_K = \sigma_h$ as

$$K = K' + h$$

where K′ is a true constant so that $\delta K = \delta h$.

For the computation of $\sigma_h = \sigma_K$ use is made of the formula

$$h = \frac{b}{a} \pm \frac{\sqrt{\overline{a\,\sigma_b}^2 + \overline{b\,\sigma_a}^2}}{a^2} = \frac{b}{a} \pm \sigma_h$$

(cf. Mellor, p. 529). From which

$$\sigma_K = \sigma_h \frac{\sqrt{\overline{a\,\sigma_b}^2 + \overline{b\,\sigma_a}^2}}{a^2} = 0.000013 \qquad (30)$$

Then as $k = 0.4343\ K$, it follows that $\sigma_k = 0.4343\ \sigma_K$.

Finally, on the basis of the formula

$$w = w' + i$$

where w′ is a true constant, we may write $\sigma_w = \sigma_i$. In computing $\sigma_w = \sigma_i$ it is convenient, first of all, to derive the deviation, σ_{aK} of the product, aK (cf. Mellor, p. 528). Thus

$$\sigma_{aK} = \sqrt{\overline{K\sigma_a}^2 + \overline{a\sigma_K}^2} = 0.0014$$

The precision of the quotient

$$i = \frac{c}{aK}$$

is then given by the formula

$$\sigma_w = \sigma_i = \frac{\sqrt{\overline{aK\sigma_c}^2 + \overline{c\sigma_{aK}}^2}}{(aK)^2} = 0.16 \qquad (31)$$

The calculation of the deviations of K, k, aK and w is shown in Table No. 4. As only 2 places of significant figures are required in weights and deviations, it will be noted that the computations of Tables III and IV may conveniently be performed with a slide-rule without introducing any appreciable error.

TABLE III

Computation of the Denominator, D_{abc} and of the Weights and Standard Deviations of a, b, and c, for the Data of Pennycuick (1926, p. 9)

Base data (rounded values; $\sigma_y = 0.11$)

$(1) = \Sigma f_1^2 = 4.42;$ $\quad (4) = \Sigma f_2 f_3 = 490.$

$(2) = \Sigma f_2^2 = 77300.\ ;$ $\quad (5) = \Sigma f_1 f_3 = 2.59$

$(3) = \Sigma f_3^2 = 7.39;$ $\quad (6) = \Sigma f_1 f_2 = 535.$

Derivation of D_{abc}

$(7) = (1) \times (4)^2 = 1{,}061{,}000$

$(8) = (2) \times (5)^2 = 519{,}000$

$(9) = (3) \times (6)^2 = 2{,}114{,}000$

$(10) = (7) + (8) + (9) = 3{,}694{,}000$

$(11) = (1) \times (2) \times (3) = 2{,}525{,}000$

$(12) = (4) \times (5) \times (6) = 679{,}000$

$(13) = (11) + (12) + (12) = 3{,}883{,}000$

$D_{abc} = (10) - (13) = -189{,}000$

Derivation of W_a and σ_a

$(14) = (4)^2 - (2) \times (3) = 331{,}000$

$W_a = D_{abc} \div (14) = 0.5710 = (0.76)^2$

$\sigma_a = \sigma_y \div \sqrt{W_a} = 0.14$

Derivation of W_b and σ_b

$(15) = (5) - (1) \times (3) = -26.0$

$W_b = D_{abc} \div (15) = 7{,}270 = (85.3)^2$

$\sigma_b = \sigma_y \div \sqrt{W_b} = 0.0013$

Derivation of W_c and σ_c

$(16) = (6)^2 - (1) \times (2) = -55{,}700$

$W_c = D_{abc} \div (16) = 3.39 = (1.84)^2$

$\sigma_c = \sigma_y \div \sqrt{W_c} = 0.060$

TABLE IV

Computation of σ_K, σ_k, σ_{aK} and σ_w

Base data (rounded values)

$a = 100.5$; $\sigma_a = 0.14$; $K = 0\ 00368$
$b = -0.000417$; $\sigma_b = 0.0013$;
$c = -0.239$; $\sigma_c = 0.060$;

Derivation of $\sigma_K = \sigma_h$ and σ_k

$(1) = \overline{a\,\sigma_h}^2 = 0.0171$
$(2) = \overline{b\,\sigma_a}^2 = 0.0000$
$(3) = (1) + (2) = 0.0171$
$(4) = (3)^{\frac{1}{2}} = 0.131$
$\sigma_K = (4) \div a^2 = 0.000013$
$\sigma_k = 0\ 4343\ \sigma_K = 0\ 0000056$

Derivation of σ_{aK}

$(5) = \overline{K\,\sigma_a}^2 = 0.000000265$
$(6) = \overline{a\,\sigma_K}^2 = .000001710$
$(7) = (5) + (6) = .000001975$
$\sigma_{aK} = (7)^{\frac{1}{2}} = .0014$

Derivation of $\sigma_w = \sigma_i$

$(8) = \overline{aK\,\sigma_c}^2 = 0\ 000492$
$(9) = \overline{c\,\sigma_{aK}}^2 = .000000$
$(10) = (8) + (9) = .000492$
$(11) = (10)^{\frac{1}{2}} = .022$
$\sigma_w = (11) \div \overline{aK}^2 = .16$

With regard to the precision actually attained, the adjusted values of the constants pertaining to the data of Pennycuick (1926, p. 9) therefore become:

$L = 100.54 \pm (\sigma_L = 0.14)$
$w = 0.65 \pm (\sigma_w = 0.16)$
$k = 0.0015982 \pm (\sigma_k = 0\ 0000056)$

Similarly, for the second set of data given by Pennycuick (1926, p. 8),

$L = 100.28 \pm (\sigma_L = 0.42)$
$w = -2.7 \pm (\sigma_w = 1.4)$
$k = 0.0006004 \pm (\sigma_k = 0.0000061)$

when all observations are considered. When one observation is omitted,

$L = 100.32 \pm (\sigma_L = 0.12)$
$w = -2.15 \pm (\sigma_w = 0.39)$
$k = 0.0006010 \pm (\sigma_k = 0.0000018)$

Deviations in L of the order of 0.1 to 0.4 per cent do not appear improbable in rate of inversion experiments, as the determination of this limiting value is the least precise of all the observations.

A deviation of one per cent or less in the value of k is indicative of a degree of precision seldom achieved in rate-of-reaction experiments (cf. Table VII, data of Daniels and Johnston, 1921).

In interpreting the significance of w in these experiments, it should be borne in mind that this quantity is not simply a time error but that it refers to the resultant effect of all constant errors on the time.

On the whole the conclusion is warranted that the unusually precise data of Pennycuick (1926) do actually conform to an equation of the unimolecular type. It would appear, therefore, that the usual methods of computation may furnish misleading results when the unimolecularity of a given process is being examined. The practical bearing of this conclusion on the various theories which have been proposed to account for apparent departures from the unimolecular formula is obvious.

Logically, the least-squares procedure should be used until the unimolecularity of a given process has either been established or disproved. If the process conforms to the unimolecular formula within known limits of experimental error, it may then appear sufficient, in the absence of large constant errors, to apply the usual methods of computation in deriving numerical values for velocity constants under various experimental conditions. The effect of disregarding constant errors will accordingly be briefly discussed.

9. Effect of disregarding Constant Errors

Let it be assumed that the constant errors in a series of observations on a unimolecular process are known to be negligibly small or else that this source of error is simply disregarded. The equation to be used will then be

$$Y = L\,(1 - e^{-Kt})$$

Now, as already shown (equation 15), the linearized form of this equation is

$$\begin{aligned} Y &= L\,(1 - e^{-K't}) + Lh\,(t'e^{-K't}) \\ &= af_1 + bf_2 \end{aligned}$$

From previous considerations, the normal equations are

$$\delta R/\delta a = \Sigma\, f_1Y - a\,\Sigma\, f_1^2 - b\,\Sigma\, f_1f_2 = 0 \qquad (32)$$

and,

$$\delta R/\delta b = \Sigma\, f_2Y - a\,\Sigma\, f_1f_2 - b\,\Sigma\, f_2^2 = 0 \qquad (33)$$

The solution of these equations gives

$$a = \frac{\Sigma\, f_2^2.\ \Sigma\, f_1Y - \Sigma\, f_1f_2.\Sigma\, f_2Y}{\Sigma\, f_1^2.\ \Sigma\, f_2^2 - (\Sigma\, f_1f_2)^2} \qquad (34)$$

$$b = \frac{\Sigma\, f_1^2.\ \Sigma f_2Y - \Sigma\, f_1f_2.\ \Sigma\, f_1Y}{\Sigma\, f_1^2.\ \Sigma\, f_2^2 - (\Sigma\, f_1f_2)^2} \qquad (35)$$

In illustration of this simplified treatment, use will be made of data given by Daniels and Johnston (1921, p. 64; their Experiment 25 at 65°C). Use has already been made of these figures in a preceding section in connection with a discussion of the "chain" formulae for the derivation of velocity constants. For the trial value of k the figure of 0.1880 will be adopted, corresponding to the highest value (K = 0.4340) given by Daniels and Johnston. The derivation of the sums demanded by equations (32) and (33) is shown in Table V. By comparison with Table I, it is apparent that, for an equal number of observations, the arithmetical work is not shortened when no allowance is made for constant errors, although subsequent computations are somewhat simplified.

TABLE V

Computations; Data of Daniels and Johnston (1921; Their Experiment No. 25)

(k′ = 0.1880; no allowance for constant errors).

t	Y	k′t	$f_3 = 10^{-k't}$	$f_1 = 1 - f_3$	f_1^2
2	18.6	0.3760	0.420727	0.579273	0.335557
3	22.6	.5640	.272898	.727102	.528677
4	25.1	.7520	.177011	.822989	.677311
5	27.2	.9400	.114815	.885185	.783552
6	29.1	1.1280	.074473	.925527	.856600
7	30.1	1.3160	.048306	.951694	.905721
Sums	152.7				4.087418

t	f_1Y	$f_2 = tf_3$	f_2^2	f_2Y	f_1f_2
2	10.77448	0.841454	0.708045	15 65104	0.487432
3	16.43250	.818694	.670260	18.50248	.595274
4	20.65702	.708044	.501326	17 77190	.582712
5	24.07703	.574075	.329562	15.61484	.508163
6	26.93284	.446838	.199664	13.00299	.413561
7	28.64599	.338142	.114340	10.17807	.321808
Sums	127 51986	3.727247	2.523197	90 72132	2.908950

By the substitution in equations (32) and (33) of the sums given in Table V, the following numerical expressions are obtained:

$$127.5199 - 4.087418a - 2.908950b = 0$$
$$90.7213 - 2.908950a - 2.523197b = 0$$

The solution of these equations gives

$$a = 31.25 = L$$
$$b = 0.07200$$

From which,

$$h = \frac{b}{L} = -0.002304$$
$$K' = 2.302585\, k' = 0.432886$$
$$K = K' + h = 0.430582$$
$$k = 0.4342945\, K = 0.1870$$

The calculated values given in the first part of Table VI were obtained by substituting the values $L = 31.25$ and $k = 0.1870$ in equation (1). By equation (18) the deviation of these values is

$$\sigma_y = \sqrt{\frac{1.09}{6-2}} = 0.52$$

Using rounded numbers, the numerical value of the denominator, D_{ab} common to equations (34) and (35) is

$$\begin{aligned} D_{ab} &= \Sigma f_1^2 . \Sigma f_2^2 - (\Sigma f_1 f_2)^2 \\ &= (4.09)(2.52) - (2.91)^2 \\ &= 10.31 - 8.47 \\ &= 1.84 \end{aligned}$$

The weights of $L = a$ and of b accordingly are

$$W_L = \frac{D_{ab}}{\Sigma f_2^2} = \frac{1.84}{2.52} = 0.730$$

and

$$W_b = \frac{D_{ab}}{\Sigma f_1^2} = \frac{1.84}{4.09} = 0.450$$

From which,

$$\sigma_L = \frac{\sigma_Y}{\sqrt{W_L}} = \frac{0.50}{0.854} = 0.585$$

$$\sigma_b = \frac{\sigma_Y}{\sqrt{W_b}} = \frac{0.50}{0.671} = 0.745$$

Then, using equation (30),

$$\sigma_K = \frac{\sqrt{L\,\overline{\sigma_b}^2 + b\,\overline{\sigma_L}^2}}{L^2} = 0.024$$

TABLE VI

Computation of σ_Y for the Data of Daniels and Johnston (1921; Their Experiment No. 25)

		Without Allowance for Constant Errors			Allowing for Constant Errors		
t	Y Observed[1]	Y′ Calc.[2]	d = Y − Y′	d^2	Y″ Calc.[3]	$d_1 =$ Y − Y″	d_1^2
2	18.6	18.0	0.6	0.36	18.7	−0.1	0.01
3	22.6	22.7	− .1	.01	22.4	.2	.04
4	25.1	25.7	− .6	.36	25.2	− .1	.01
5	27.2	27.6	− .4	.16	27.3	− .1	.01
6	29.1	28.9	.2	.04	28.9	.2	.04
7	30.1	29.7	.4	.16	30.1	.0	.00
			$\Sigma d^2 = 1.09$			$\Sigma d_1^2 = 0.11$	

---

[1] Values reported by Daniels and Johnston (1921, p. 64).

[2] Using equation (1); $L = 31.25$; $K = 0.43058$ ($k = 0.1870$).

[3] Using equation (5); $L = 33.805$; $K = 0.28361$ ($k = 0.12317$); $w = 0.8317$.

When no allowance is made for constant errors, the most probable values of L and K for the data in question (Experiment 25 by Daniels and Johnston, 1921) may therefore be written

$$L = 31.25 \pm (\sigma_L = 0.59)$$
$$K = 0.431 \pm (\sigma_K = 0.024)$$

The value of L given by Daniels and Johnston (1921, p. 64) is 32.6. For the value of the velocity constant they deduce K = 0.345 while in their experiments 23 and 24 at the same temperature they report the values 0.290 and 0.293, respectively. Commenting on these results, Daniels and Johnston (1921, p. 65) state: "The velocity constant in Experiment 25 does not check with the others at the same temperature. The errors in it, however, are greatly magnified because the experiment was carried out at a very low pressure in order to contrast it with Experiment 25 in which a high pressure was used. * * * Accordingly, it is excluded in determining the average velocity constant at 65°C."

For purposes of comparison the calculated values which are obtained when proper allowance is made for constant errors are also given in Table No. 6 (Column headed Y″). The deviation of this second set of values from the values observed in Experiment 25 by Daniels and Johnston is

$$\sigma_y = \sqrt{\frac{0.11}{6-3}} = 0.19$$

By inspection, the agreement between the observed and calculated values (Y and Y″) is excellent. It will also be noted that the velocity constant which pertains to this recalculation (K = 0.28361, corresponding to k = 0.12317; see footnote, Table No. 6) is in good agreement with the values (0.290 and 0.293) obtained by Daniels and Johnston in their Experiments 23 and 24. The discrepancy between the observed and calculated values of L (32.6 and 33.805, respectively) is reflected by the relatively high value of w = 0.8317.

On the basis of the agreement between the observed and calculated values, it would appear unnecessary to reject this series of observations although, as will be shown elsewhere*, the weight of this particular series of observations is so small that its omission is without material effect on the general average.

In Table VII the most probable values (in the sense of least-squares) of the velocity constants recalculated from the data of Daniels and Johnston (1921) are compared with the values actually reported by these experimenters. Excluding Experiment 25, the difference between the two sets of constants varies from 0.5 to 12.6 per cent. With less precise data, much greater differences would be observed. If the velocity constants deduced by least-squares are accepted as most representative of the observations, it must be concluded that the use of the least-squares procedure is the mathematical equivalent of such analytical safeguards as precise temperature control, refined manometric technique, etc. In fact, the difference noted in Table VII are equivalent, on the whole, to temperature variations of 0.1 to 0.2°C., while, as stated by Daniels and Johnston (1921, p. 65), "The thermostat was constant to 0.03°."

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* It is expected that the data of Daniels and Johnston (1921) will be more fully discussed in a separate paper bearing on the statistical treatment of the Arrhenius expression for the dependence of velocity constants on temperature.

TABLE VII

A Comparison of the Velocity Constants deduced by Least-Squares with the Constants reported by Daniels and Johnston (1921)

Experiment Number	$K \times 10^3$ (Least-Squares)	$K_1 \times 10^3$ Daniels and Johnston	Percentage difference $\frac{100(K - K_1)}{K}$
	At 27°C.		
2	2.120	2.14	− 0.9
3	2.020	2.01	0.5
12	2.017	1.93	4.3
	At 35°C.		
5	7.959	7.89	0.9
6	7.84	8.83	−12.6
11	7.821	7.54	3.6
	At 45°C.		
7	28.43	29.4	− 3.4
8	27.76	29.3	− 5.5
9	29.20	30.9	− 5.8
	At 55°C.		
15	91.7	89.2	2.7
26	92.44	90.9	1.7
	At 65°C.		
23	268.8	290.	− 7.9
24	282.0	293	− 3.9
25	284.0	345[1]	−21.5

[1] This result rejected by Daniels and Johnston (1921).

Summary

1. A statistical treatment applicable to unimolecular data has been developed. The procedure makes it unnecessary to determine experimentally the value of L in the unimolecular formula

$$K = \frac{1}{t-t_o} \ln \frac{(L-Y_o)}{(L-Y\ )}$$

Also, as proper allowance is made for constant errors in Y and t, the quantities Y_0 and t_0 need not be accurately known. Instead of a series of K values, only one properly-weighted velocity constant is obtained.

2. It has been shown that the data of Pennycuick (1926) on the inversion of sucrose do actually conform very closely to an equation of the unimolecular type.

3. In general, the usual methods of computation will furnish misleading indications when the unimolecularity of a given process is being examined.

4. The velocity constants given by Daniels and Johnston (1921) for the rate of decomposition of nitrogen pentoxide have been recalculated. The least-squares values of the velocity constants differ by 0.5 to 12.6 per cent from the values given by Daniels and Johnston.

5. The conclusion is warranted that adherence to the usual methods of computation is inconsistent with refinements of analytical technique. The least-squares procedure should be used whenever a velocity constant is to be determined within an allowable error of, say, 5 per cent.

THE EFFECT OF GELATIN AND SALTS ON CONGO RED*

BY HERBERT L. DAIVS AND JOHN W. ACKERMAN

In the practical application of colloid chemistry no property is more often used than that shown by a number of usually lyophilic colloidal substances by virtue of which they are able to stabilize other colloids, which are for the most part lyophobic. Many examples of this protective action are known and have been studied; but the student of these phenomena can not proceed very far before coming to the point beyond which our knowledge has not gone. This paper will present a contribution to this problem by showing that in certain systems containing gelatin and Congo red in which we should expect a protective action, the phenomena are for the most part to be interpreted on the assumption of an independent existence of these two substances in the mixed sols and only under special conditions does anything like protective action appear and then in a form not usually associated with these phenomena.

A definition of protective action has been given by Thomas:[1] "When a solution of a hydrophilic colloid is added to a less stable dispersion, or suspension, generally there is no change in appearance of the system and the less stable dispersion is found to have become more stable, i.e., it is no longer so sensitive toward coagulation by either the addition of electrolytes or by evaporation to dryness. The less stable dispersion is said to have been 'protected' by the hydrophilic colloid; hence the term 'protective colloid,' which is commonly applied to the hydrophilic colloids, such as gelatin, gum arabic, albumin, etc."

But the addition of gelatin to another colloid is often a much more complex phenomenon than would appear from this simple definition and the literature shows several cases of sensitizations such as are discussed by Bancroft.[2]

"Since a colloid peptized by water may be charged positively or negatively, there is no reason why it should not precipitate another colloid under suitable conditions. We usually consider the colloids peptized by water solely as protecting colloids, but this is clearly an inadequate view, as is shown by the experimental data. Years ago Schulze[3] pointed out that small amounts of gelatin solutions were as effective as lime or alum in causing the rapid sedimentation of clay, and that addition of minute quantities of gelatin to barium sulphate simplified the question of washing and filtration very much. He, of course, gave no adequate explanation of the phenomenon and the real explanation was given by Billitzer,[1] who called attention to the fact that, while gelatin, agar-agar, etc., ordinarily check the precipitation of colloidal solutions, by electrolytes, small amounts of these same substances may have a precipitating action. This can be detected even when the gelatin produces no precipitation itself. Billitzer cites the experiments of Neisser and Friedemann in which it was found that a mastic emulsion containing a trace of gelatin was precipitated more readily by sodium chloride than when no gelatin is present.[2] Billitzer finds that gelatin precipitated such negative colloids as antimony sulphide and arsenious sulphide in acid or neutral solution, but does not precipitate positively charged sols such as hydrous ferric oxide, Gelatin in ammoniacal solution precipitates hydrous ferric oxide, though no precipitation occurs if ammonia is added to a mixture of gelatin and ferric oxide. Bismarck brown, which is a positive colloid, is precipitated by an alkaline gelatin solution, while eosine is precipitated by an acidified gelatin solution."

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* This work is part of the programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Bogue: "The Theory and Application of Colloidal Behavior," 1, 346 (1924).

[2] "Applied Colloid Chemistry," 309 (1926).

[3] Pogg. Ann., 129, 369 (1866).

A little later, p. 311, Bancroft returns to the more usual protective action and the measure of it. "Coming back to the general problem, if the ratio of gelatin to the other colloid is increased sufficiently, we shall pass through the precipitation range into the range where the colloidal solution is stabilized by gelatin and then behaves more like a water-soluble colloid. Colloidal gold and colloidal silver solutions, when stabilized by gelatin, can be evaporated and redissolved, because the gelatin prevents the irreversible agglomeration. When less gelatin is used it may retard, though not prevent, the change of red colloidal gold to blue. Zsigmondy[3] defines as the gold number the number of milligrams of a protecting colloid which just prevents the color change in a 10 cc red gold solution, containing 0.0053-0.0058 percent gold, when one cubic centimeter of a ten percent sodium chloride solution is added. Of course, a strongly adsorbed non-electrolyte, such as sugar, will act similarly to gelatin; but, in most cases, the adsorption is so much less that these substances are only interesting theoretically as stabilizers."

It is quite generally agreed that the protective action is due to the formation of an envelope or sheath of the protective colloid about the particles of the protected dispersion. As a result of this it is found that the conduct of the coated particles is identical with that of a solution of the protective colloid. This was shown by Loeb[4] who found that collodion suspensions to which gelatin and other protein sols were added lost the properties of the collodion and behaved as sols of the protein alone toward salts, cataphoresis, isoelectric point, etc. In certain cases there was poor protective action and in others there was slight deviation of the properties of the mixed sols from that of the protector, such as in the case of albumin where Loeb believed adsorption on the collodion particles produced an effect analogous to the so-called denaturation of the albumin. But as a general rule a substance which is to act as a protective colloid must be strongly adsorbed by the dispersion to be protected and will impart to the mixture properties of the protecting sol. Contrary to expectation gelatin is but weakly adsorbed by Congo red and the properties of the mixed sols are those of both of its components. Especially prominent among the latter are the properties of dyeing cloth by the mixed sols in the presence of various salts.

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[1] Z. physik. Chem., **51**, 145 (1905).

[2] Cf. Walpole: J. Physiol., **47**, xiv (1913); Biochem. J., **8**, 170 (1914).

[3] Z. anal. Chem., **40**, 697 (1901).

[4] J. Gen. Physiol., **5**, 479 (1922-3).

The first direct evidence of this state of affairs was the behavior of gelatin swelling in dilute solutions of Congo red. When one gram of powdered gelatin is added to fifty cc of 0.006% solution of Congo red, the swelling gelatin at room temperature is found to contain but little more dye on or within its particles than does the clear supernatant solution which is in turn only slightly lighter than a blank solution to which no gelatin was added. This indicates very clearly that little or no protective action should be expected.

The Effect of Salts on Congo Red Solutions

In spite of the very slight adsorption shown by the Congo red and gelatin there are some phenomena which would ordinarily be interpreted as showing protection. Before proceeding to them it will be well to show some of the properties of the Congo red itself, since these properties indicate Congo red to be somewhat intermediate between the lyophobe and lyophile classifications of colloidal substances. In the first place it can be precipitated by suitable concentrations of sodium and potassium chlorides and iodides. In all these experiments a stock solution containing two grams of Congo red in a liter of solution was employed, usually by adding five cc of the stock solution to sufficient of the other reagents to make 25 cc. The dye solution as diluted finally, then, was 0.04%; samples of 0.01 and 0.02 mol of the halides were dissolved in 20 cc of solution and added to five cc of the stock Congo red. In these low concentrations of salts the precipitation was slow so that the final observations were made after 45 hours. In the case of the solutions which were 0.8 M with respect to the salts the differences were less than in the case of those 0.4 M, for in the more concentrated solution precipitation of the Congo red was nearly complete. Comparison of the precipitates and the supernatant solutions showed, however, that in both dilute and concentrated solutions the effect was in order $KI > KCl > NaI > NaCl$, the potassium iodide having the greatest precipitating effect and the sodium chloride the least effect. This shows that the iodides are more effective than the corresponding chlorides and that the potassium salts are more effective than the sodium salts. The fact that potassium chloride has greater precipitating power for Congo red than sodium iodide has shows that the difference between the metallic ions is greater than that between the chloride and iodide ions. This suggests a Hofmeister series for the coagulation of the negatively charged Congo red micelle[1] and the experiment showed that 0.4 M $BaCl_2$, when added as above, precipitates Congo red almost at once, leaving a clear, colorless, supernatant liquid after ten minutes. In respect to its behavior with salts Congo red acts like a typical lyophobe colloid; but it is readily peptized by water alone and this is a property more often found in lyophile colloids.

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[1] Weiser and Radcliffe: J. Phys. Chem., 32, 1875 (1928).

The experiments with sodium chloride were continued to greater concentrations and it appears that these systems show a phenomenon akin to the "irregular series." Systems of 25 cc each were made up, each containing five cc of the stock Congo red and sufficient 5N NaCl to make them one, two, three, and four normal with respect to the salt. Although the 4N NaCl system grew quite turbid at once and was soon completely coagulated, the 2N NaCl produced finally much less precipitation of the Congo red than did either the 1N or the 3N systems. Further experiments confirmed this and showed that there is a broad minimum in the coagulating power of sodium chloride when the salt concentration is 1.4–1.6N; systems 1.4–2.0N are not greatly coagulated on standing for several days while systems containing more or less salt are practically completely coagulated and precipitated. This appears to be a case of irregular series as discussed by Kruyt.[1]

"The phenomena observed when a sol is flocculated by means of an electrolyte such as $AlCl_3$ agree well with the changes in boundary potential. When increasing amounts of $AlCl_3$ are added to a negatively charged sol of mastic, we notice that small concentrations cause flocculation, somewhat higher concentrations produce another stable sol of opposite sign, i.e., positively charged, while still higher concentrations bring about another flocculation. . . .

"We have, therefore, first a non-flocculation zone; but as soon as the negative critical potential is reached, flocculation begins. This primary flocculation zone ends when, after reversal of the charge, the positive critical potential is attained. From that concentration on, the $AlCl_3$, instead of causing flocculation exerts a recharging action. Hence the mastic sol is positively charged in this second zone of non-flocculation. But, positive boundary layers are discharged by anions and the positive potential, after going through a maximum value, is reduced by the Cl ions until the critical potential is reached. At that point, a second flocculation zone begins.

"This phenomenon is designated as an *irregular series.* It will always occur when the potential-lowering effect of the cation is far in excess of the potential-raising effect of the anion. This lowering effect may be due either to a high valence of the ion or to a high degree of adsorbability. Polyvalent cations give, therefore, irregular series when they are combined with monovalent anions. But monovalent organic cations act in the same way. For instance, strychnine nitrate, as well as new fuchsin, yields an irregular series with As_2S_3 sol, and $AgNO_3$ with the sol of HgS, because in each case the cation is strongly adsorbed.

"A converse reasoning applies to positively charged sols. Here the anion discharges, while the cation may raise the charge. Whenever there is a great contrast between the two ions, an irregular series will occur; hence we readily understand why the positively charged sol of iron oxide forms an irregular series with sodium phosphate (monovalent cation *vs.* trivalent anion), and with NaOH (monovalent ions, but anion strongly adsorbable)."

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[1] "Colloids," 89 (1930).

The Congo red sol does not exactly fit this picture, for cataphoresis on the system that was 1.5N NaCl showed that in this zone of non-coagulation the sol is negatively charged as it is in the salt-free condition. In addition to this, small additions of $BaCl_2$ solutions caused immediate turbidity and rapid flocculation and precipitation of the dye in the 1.5N NaCl; systems that were 1.5N NaCl and 0.1N $BaCl_2$ were coagulated somewhat less rapidly but not less completely than systems containing only dye and 0.1N $BaCl_2$. On the other hand, additions of sodium sulphate had no effect on the sodium chloride-Congo red systems except to clear up a slight turbidity produced by the sodium chloride on the dye. If the sol in the non-flocculation zone were positively charged, cataphoresis should have shown it and the sol should have been coagulated on the addition of sodium sulphate instead of barium chloride.

We have here, apparently, an irregular series without the reversal of charge on the colloid. This must be due to a higher adsorbability of the sodium ions on the Congo red, the difference between the adsorbabilities of the sodium and chloride ions being too small to permit a reversal of the charge. The first addition of sodium chloride results in preferential adsorption of positive sodium ions and the reduction of the charge on the Congo red micelles below the critical value. Higher salt concentrations give also some adsorption of chloride ions sufficient to raise the potential above the critical value; and finally sufficient excess of sodium ions are adsorbed to reduce the potential again below the critical value and produce precipitation.

It may be added that sodium sulphate also appears to give with Congo red such an irregular series as is shown by sodium chloride. Molar sodium sulphate produces markedly less coagulation and precipitation than do systems 0.5 or 0.75 M with sodium sulphate.

It has been shown that Congo red may be precipitated by various salts in the proper concentrations. The addition of gelatin to such systems results in a great decrease in the flocculating power of the salts. Systems containing the regular amount of five cc of the stock Congo red solution, sufficient sodium chloride to make them 3.1 and 4.8N respectively, and without or with the addition of five cc of two percent gelatin solution gave the following results in two hours:

	3.1N NaCl	4.8N NaCl
Without gelatin	greatly coagulated	completely coagulated
With gelatin	quite clear	slightly turbid

Solutions of gelatin protected also against precipitation by barium chloride, for whereas 0.1N $BaCl_2$ precipitates the dye rapidly and completely at room temperature, 0.8N $BaCl_2$ produced no observable effect on Congo red in presence of gelatin, even at 95° for an hour. Another experiment with potassium iodide showed that in systems containing up to N KI there was increasing precipitation of the dye while in similar systems containing gelatin there was no coagulation.

These results are typical of the behavior of the dye in the presence of gelatin and one would be inclined to interpret them on the basis of protective action by the gelatin. But if there be little adsorptive attraction between the gelatin and the dye, there can be little protective action and this has been shown to be the case in the absence of salts. In the presence of salts however there does appear to be adsorption of the dye by the gelatin which will explain these phenomena. To demonstrate this, six mixtures were made up, each containing 50 cc of 0.006% Congo red and to this was added the powdered gelatin and the sodium sulphate as shown below.

	A	B	C	D	E	F
Powdered gelatin	0	one gram	0	one gram	0	one gram
Mols of Na_2SO_4	0	0	0.01	0.01	0.02	0.02

Sodium sulphate was chosen because it had been found very effective in salting the dye out of solution, and also because the gelatin would swell less in its solution than in the presence of the halides. The powdered gelatin did swell in all the solutions and took up dye from the solution, comparison of A and B showing that. The addition of salt in C gave a lighter solution than the blank A and for the moment it will be assumed that this change of color is associated with an increase in the size of the colloidal micelles of the Congo red since, of course, there can be no adsorption to decrease the concentration of the dye in the solution and it has already been shown that the addition of more sodium sulphate completes the agglomeration of the dye into particles so large that they are precipitated. The supernatant solution in E is also lighter than that in A but no precipitation of the dye takes place even on long standing. The swelling gelatin in D and F is increasingly darker with the adsorbed dye than is the gelatin in B, and the remaining solution in D and F is increasingly lighter than that in A showing that the gelatin in the presence of increasing amounts of sodium sulphate is adsorbing increasing amounts of the Congo red, or that the salt in concentrations that would otherwise not precipitate the dye can nevertheless cause it to be adsorbed on the gelatin. In the next section it will be shown that the addition of salts causes the dye to be adsorbed more strongly on cloths also. It is not possible to coagulate the dye alone from a system containing 0.04% Congo red and 0.4% gelatin by means of sodium sulphate, for any concentration of this salt that will have any effect is more than the half-saturated solution at which gelatin alone is coagulated and thus carries down the dye with it. The case under discussion is, however, not a case of the carrying down of the dye by the swelling gelatin for there is a definite difference between the systems containing salt and those without the sodium sulphate, the same amount of gelatin being present in each. Further than that, if it were merely a case of filter action, continued shaking should remove all the dye from solution whereas this is not the case. There is a rapid adsorption of the dye on the gelatin which then reaches an adsorption equilibrium leaving a large proportion of the dye still in solution. The final condition is independent of the order of mixing the dye, gelatin, and salt solution.

The assumption introduced above, i.e., that the change of color of the Congo red solution on adding sodium sulphate solution and the increased adsorptive attraction between the altered dye sol and the gelatin are accompanied by a decrease in the dispersion of the dye is not without support in the literature although it is not generally expressed so explicitly. Bancroft[1] discusses the problem in these terms: "With colloids stabilized by an electric charge, we find that the amount of salt necessary to produce precipitation varies with the way in which it is added, more being necessary if the salt solution is added slowly.[2] The precipitation value obtained by adding the electrolyte all at once is such a concentration of the precipitating ion that sufficient adsorption to cause neutralization can result in a definite time. Weiser[3] considers that if the same amount of electrolyte is added very slowly, there results a gradual increase in the size of the particles due to partial neutralization by adsorption. After the addition of enough electrolyte, partial agglomeration takes place. These coagulated particles have adsorbed not only enough to effect their complete neutralization; but the neutralized particles have carried down an additional amount during agglomeration. This adsorption of electrically neutral particles during the fractional precipitation accompanying slow addition of the electrolyte causes such a decrease in the ionic concentration that a greater amount must be added to effect complete neutralization by this fractional process. Rapid addition furnishes at once all the critical concentration of precipitating ion necessary for neutralization by adsorption."

In the experiments reported above, the addition of the precipitating salts has been made all at once, so that question does not enter here. It is suggested however that the addition of the sodium sulphate makes the Congo red particles more instable and therefore more easily adsorbed on the gelatin, which if it were peptized would tend to prevent the precipitation of the dye and thus give the appearance of protection without the existence of any gelatin envelope before the addition of the salt. This problem has been further discussed by Bancroft, p. 299.

"Making a colloidal solution instable will increase the amount of adsorption by a solid adsorbent until the agglomeration of the colloidal particles becomes too great, when the large particles will not be held firmly by the adsorbent. This principle is made use of in dyeing with substantive dyes.[4] Substantive dyes dye cotton direct without a mordant. They are usually sodium salts of color acids and are always in colloidal solution. They are taken up as salts and not as color acids by the fibers. Sodium chloride, sodium sulphate, and sodium citrate increase the amount of dye forced on the fiber when these salts are used in moderate concentrations. At higher concentrations they strip the dye. Sodium sulphate, therefore, decreases the adsorption of an acid dye by wool and increases the adsorption of a substantive dye by wool or cotton. In both cases the color is in the acid radical; but the acid dye is in true solution and it is the color acid which is adsorbed, while the substantive dye is in colloidal solution and it is the salt which is adsorbed."

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[1] Bancroft: "Applied Colloid Chemistry," 296 (1926).

[2] Freundlich: Z. physik. Chem., **44**, 143 (1903).

[3] Weiser: J. Phys. Chem., **25**, 404 (1921).

[4] Briggs: J. Phys. Chem., **28**, 368 (1924).

Considering the first sentence of the above quotation, it appears obvious that the increase in particle size does not suddenly begin and all take place just at the moment of coagulation or at the concentration at which the particles become too large to be held firmly by the adsorbent. Increase in particle size must begin with the first addition of the precipitating agent and be responsible for the observed increase in adsorbability. In other words the slowly coagulating particle shows an enhanced readiness to adsorb nearly anything such as colloidal substances which would tend to keep it suspended, or, failing that, solid adsorbents such as cloths to be dyed. The drowning man grasps at the straw which would have proved no attraction whatever while he was well able to keep himself afloat. This may be the explanation for the slow precipitations so often observed. Some particles are neutralized by the electrolyte and in turn adsorb other relatively unaffected and stable particles. The particle size thus increases while the charge ratio diminishes until particles grow large enough to be seen and finally settle out.

The theory of dyeing with substantive dyes was formulated and summarized by Briggs in the paper referred to above. In his discussion of the properties of aqueous solutions of these dyes (p. 370), Briggs says: "The dialyzed solutions, like those of the soaps, are excellent conductors; they exert in a collodion osmometer a surprisingly high apparent osmotic pressure; in the absence of a membrane they possess an easily measurable power of diffusion; and they invariably contain amicrons or ultramicrons when viewed in the ultramicroscope. It is possible to bring about an increase in the size of the ultramicrons and a corresponding decrease in the degree of dispersion, without causing any visible or actual flocculation of the suspended dye—a property of the substantive dye solutions which is of the utmost significance in the theory of substantive dyeing. Increase in the size of aggregates is observed as the concentration of the dye is increased, or as the temperature is lowered; at low temperatures concentrated solutions of the substantive dyes set to a jelly. Decreased dispersion is also caused by destabilizing electrolytes, while electrolytes in excess bring about flocculation.[1] The growth of aggregates is opposed by stabilizing protective colloids such as gelatin.[2] Practically all of the very complete evidence now available supports the conclusion that in neutral or alkaline dyebaths the substantive dyes are present as electronegative colloids capable of a very high degree of dispersion in the absence of destabilizing agents.

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[1] Cf. Biltz and von Vegesack: Z. physik. Chem., **73**, 481 (1910); Wo. Ostwald: Kolloidchem. Beihefte, **10**, 197 (1919); Auerbach: Kolloid-Z., **31**, 37 (1922).

[2] Cf. Bayliss: Kolloid-Z., **6**, 23 (1910); also Biochem. J., **1**, 175 (1906).

"While a flocculating agent will tend to force the suspended colloid into the interface, it should not be present in amounts large enough to produce actual coagulation. If the latter occurs, the agglomerated flocks may be too large to be retained in the interface and will therefore not be adsorbed, at least strongly. Since flocculating agents in amounts insufficient to produce actual coagulation are known[1] to destabilize sols by decreasing their dispersion, such agents will aid in the adsorption of a colloid up to the point of flocculation but beyond this point will act in an opposite direction. The amount of adsorbed colloid in the interface will therefore pass through a *maximum* as the concentration of the flocculating substance is increased beyond its coagulating value. Such adsorption maxima have been observed and they show, in reality, that a dispersed colloid is most strongly adsorbed when its dispersion has some intermediate value, as Wo. Ostwald[2] has suggested.

"Flocculating agents are not the only cause of decreased stability and correspondingly increased adsorption within limits, for the stability of a sol may change with the temperature, with age, and with its previous history. The stability and the dispersion decrease with increase in the concentration of the sol, which may have something to do with the fact, which has puzzled some of us, that more is adsorbed from a concentrated sol than from a dilute one, and the adsorption curve looks like the typical isotherm obtained with a dissolved adsorbed substance,[3] p. 372.

"In terms of the present theory, an acid, base, or salt which acts as an assistant in the substantive dyebath does so because it makes the particles of dye more strongly interfacial between bath and fiber. This in turn it accomplishes by decreasing the dispersion and stability of the dye in the suspension or sol which constitutes the bath. We have seen that electrolytes are known to produce this effect in the case of various organic colloids in suspension and we should expect the same effect with colloidal dyes. Many instances are indeed known, especially among the experiments of Dreaper and his coworkers.[4] Bayliss[5] found that the addition of two percent of sodium chloride to a weak suspension of Congo red trebled the adsorption of this dye by filter paper. Concerning the effect of this salt, he wrote as follows: 'Notwithstanding the fact that no actual precipitation takes place in these experiments, the addition of electrolytes to Congo red, for example, causes an increase in the size of the colloidal particles. . . . so that the solution is on its way to precipitation even when this does not actually occur. The specimen of Congo red used in all my experiments showed the Tyndall phenomenon very faintly in solution in distilled water; but when sodium chloride was added the beam of light became much more distinct.' . . . The agglomerating and destabilizing action of weak flocculating agents in solutions of the substantive dyes may be regarded as absolutely established at the present time," p. 376.

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[1] Note Linder and Picton's work on the "degradation" of arsenious sulphide sols by sodium chloride. J. Chem. Soc., **67**, 73 (1895).

[2] "Grundriss der Kolloidchemie," 417 (1910). Cf. Traube and Shikata: Kolloid-Z., **32**, 316 (1923).

[3] Cf. Briggs: J. Phys. Chem., **19**, 210 (1915).

[4] Dreaper: "Chemistry and Physics of Dyeing," 251 et seq (1906).

[5] Biochem. J., **1**, 175 (1906).

Kraemer in his chapter[1] on "Colloids" points out some cases of this;

"In many cases a relatively slight aggregation occurs without continuing through the stages of complete coagulation, i.e., an aggregate of primary particles may possess a normal degree of stability. The red-to-blue color change in Faraday gold sols upon the addition of insufficient electrolyte to precipitate them is due to such a partial aggregation. Another is the spontaneous formation of 'tactosols' (aged sols of V_2O_5, Fe_2O_3 or benzopurpurin united into loose swarms) already referred to. Varying degrees of partial aggregation also likely occur in the high-viscosity lyophilic dispersions. Rather direct evidence of such a condition is provided by the rigidity and elasticity, on a microscopic scale, of apparently fluid sols of gelatin or soap."

But the experimental evidence in favor of this view is not universally accepted and that on the gold sols may or may not be true. Therefore it is quite interesting that another method of investigation has brought substantiation to the views here advanced. These experiments have to do with the addition of aluminum sulphate, aluminum nitrate or magnesium sulphate to sols of gold, gum mastic or arsenic trisulphide. Burton and Annetts[2] say:

"The original intention in the present experiments was to use the changes in scattered light to follow changes in samples of colloid to which extremely small amounts of various electrolytes had been added. These results led to the complementary experiment of testing the effects of the coagulation process on the light transmitted by a sample of colloid. The latter in turn led to the discovery of the existence of apparently permanent stages of partial coagulation which do not appear to have been accentuated before." Items in the summary of this paper include: "(1) Experiments have been carried out on the measurement of scattered light and transmitted light from samples of colloidal solutions. These give indication of distinct changes in the colloid on the addition of very small traces of electrolyte even before coagulation sets in. (2) By adding successively very small traces of electrolyte to solutions of gold, mastic and arsenious sulphide, the existence of stages of partial coagulation has been demonstrated." This idea has also appealed to Mullin[3] for he says:

"It is a heretofore unexpected fact, possibly not at all characteristic of dyeing acetate silk only, that certain compounds (dyestuffs) have a much greater affinity for acetate silk when in colloidal solution, possibly in even a rather coarse dispersion, than when they are in true solution. This is particularly the case where the compound is solubilized by means of chemical combination with some solubilizing reagent, such as the solubilization of certain bases by means of hydrochloric acid to form their hydrochlorides, or by sulfonation." A little later we find: "If we neutralize an aqueous base-hydrochloride solution with an alkali such as sodium carbonate, the free base is precipitated as a colloidal or even coarser dispersion in the bath and this free base is rapidly taken up by the acetate silk, as was mentioned in connection with the application of bases for the developed colors on acetate silk, and we get much deeper shades than where we depend only upon the hydrolysis of the dyestuff (base-hydrochloride) to dye the fiber."

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[1] Taylor: "A Treatise on Physical Chemistry," **2**, 1695 (1931).

[2] Burton and Annetts: J. Phys. Chem., **35**, 48 (1931).

[3] Mullin: "Acetate Silk and its Dyes," 278 (1927).

Now, obviously, the change in particle size is not the only condition that is changing here since, for instance, in the case of Mullin's dye-hydrochloride adsorption, the addition of sodium carbonate will have a large effect in increasing the hydroxyl ion concentration of the solution and such an increase would, of course, increase greatly the adsorption of the free dye base. Likewise, the addition of salts may have a similar effect on the adsorption of Congo red on the gelatin or cloths. It will be impossible to discover whether increased particle size or the changed ionic environment is responsible for the increased adsorbability until some ready method can be evolved for changing the one of the factors without affecting the other. Boiling effects the coagulation of many sols and we know that, in general, adsorption, such as dyeing, takes place more rapidly in warm solutions. Unless the stages of such coagulation are spontaneously reversed on cooling, cloths should take up increasing amounts of dye from sols that have been boiled for increasing periods and then cooled to room temperature and this should hold nearly to the point of complete precipitation. Increased particle size appears to be the one factor common to increased adsorbability.

Another instance of the protective power of gelatin for Congo red is found in acidifying the solution. Congo red is an indicator changing from red in alkali to blue in acid solution (pH range 3.0-4.0). Addition of hydrochloric acid effects an immediate development of the blue color and a rapid and complete coagulation of the dye. Such a solution gives at once a clear colorless filtrate. If sufficient gelatin be added to the dye to make the final solution 0.4%, the final dye concentration being 0.04%, the addition of sufficient hydrochloric acid to make the final system 0.16N produces as before the deep blue color but no precipitation and the blue sol is stable indefinitely. Boiling for ten minutes, however, coagulates the blue sol completely, and the clear, colorless filtrate appears to have lost permanently the power to protect Congo red from precipitation by acid. If this filtrate be cooled and neutralized, and to it are added new amounts of Congo red and hydrochloric acid immediate coagulation results. This coagulation cannot be due to the sodium chloride produced in neutralization for such a concentration would have no effect on a normally protected sol and did not produce any effect before the addition of the acid. It seems scarcely likely that the dye precipitated in the first instance should have carried down all or practically all the gelatin present.

Dyeing with Congo Red

In recent attempts to dye with certain water-insoluble dyes formed in and protected from precipitation by gelatin, the difficulty was encountered that such sols would not dye satisfactorily, the dye being taken up too little or washing off too easily. This could have but two possible explanations; either the dye sols were dispersions so coarse that sufficient penetration into the fiber was impossible, or the gelatin was being adsorbed with the dye, cutting down the adsorption of the dye itself and also facilitating its removal during the washing process. The latter seemed the more probable explanation and to test this the same procedure was applied to a substantive dye for cotton and one which was therefore known to be fine enough to penetrate properly and to be adsorbed strongly. Gelatin should diminish the adsorption and the fastness to washing of such a dye and methods which might be found to destroy the effects of the gelatin on the ordinary substantive dye should be effective also in making possible satisfactory dyeing with the insoluble dye protected by gelatin.

This procedure had a flaw in its premise and it appears worth while to report the discovery of that flaw while the solution of the main problem is still being sought. The flaw is that at least in the case of Congo red, the substantive dye selected, gelatin does not form a protective film about the dye particles but the two stable sols exist in the mixture as independent colloidal particles, and only under special conditions such as on the addition of salts does any phenomenon such as protection make its appearance. It is found that gelatin swelling in a Congo red solution has but little power to adsorb the dye but that this adsorption is increased somewhat by the addition of suitable salts. If, therefore, the gelatin and the Congo red exist independently in the solution, this is quite a different situation from that which prevails in the case of the para red, an insoluble developed dye which may be protected from precipitation by forming it in the presence of gelatin when the particles of the dye must surely be surrounded by an envelope of gelatin. The problem of breaking such a sheath in such a way as to cause the enclosed dye to be adsorbed on the cloth is quite different from that involved in bringing about the precipitation of dye rather than gelatin from a mixture of the sols.

The Congo red used in the experiments was dissolved two grams in a liter to make the stock solution, and five cc of this added to gelatin, salt, etc., to make 25 cc total volume, the final dye concentration being 0.04%. The gelatin was a powder from Baker and was usually dissolved to make a two percent solution shortly before use; five cc of this solution in the 25 cc gave a final concentration of 0.4% gelatin. The usual procedure was to immerse the cloths for one hour, dry, divide the cloth, and thoroughly soap one half and wash it in warm water.

The first experiments showed that at room temperature pieces of cloth immersed for one hour were dyed much more deeply in the absence of gelatin than in its presence. This is in agreement with the findings of Briggs[1] with other substantive dyes. He showed that this action of the gelatin is opposite to the action of salt and made a rough measurement of the effect. In connection with this it is interesting to find that in the absence of gelatin, the addition of sodium chloride resulted in increasing dyeing up to a concentration of 0.25 M. Increased salt concentration caused decreased dyeing until at 4 M approximately half the maximum amount of dye was adsorbed. The dye used in this experiment was Erie Red 4B.

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[1] Briggs: J. Phys. Chem., **28**, 384 (1924).

This decrease in dyeing from the 0.4% gelatin-dye sols did not appear when the cloths were dyed at 70°. In the hot solutions the cloths were dyed two to three times more deeply than at room temperature but the difference due to the gelatin was very slight. This effect of the gelatin in the cold solutions is to be ascribed to a blocking effect whereby the gelatin rather than the dye is adsorbed on the cloth. In the hot solutions the penetration of the dye is increased and its stability is decreased with consequent increase in the amount adsorbed by the cloth. Likewise, in the hot solutions the gelatin tends to be peptized, and can thus offer less blocking effect to prevent the dye adsorption. If this is the explanation, the blocking effect might be observable even at higher temperatures if larger quantities of gelatin were present. This was found to be true, for when cotton was dyed at 70° in solutions containing the same amount of dye dissolved in water only or in the presence of 10% gelatin the cloth dyeing in the gelatin system adsorbed much less dye than the one in water only.

The Effect of Salts on Congo Red Dyeing

In the attempt to destroy the effect of gelatin on the dyeing with Congo red, the addition of salts was the first expedient. The effect of salts should be a dual one, on the dye and on the gelatin. As has been shown above, several salts are able to bring about the more or less complete coagulation of Congo red and, as Briggs[1] showed, substances thus effective may be used for the partial destabilization of the sols of such substantive dyes, producing decreasing dispersion and increasing adsorption of the dye by the cloth. The salts employed may be classified roughly into those which exert a liquefying or peptizing action on the gelatin, such as the halides and alkalies, and those which raise the gelation point, such as sodium sulphate.

All of the salts employed of either class have a definite action in forcing the Congo red on cotton. But the portion of dye thus forced on by the salt, either with or without the addition of gelatin, does not penetrate so well nor adhere so firmly as the dye put on from the aqueous sol alone. This is shown by the fact that cloths dyed in the presence of salts are found to be made up of threads which are alternately light (or white) and dark, the light places being those areas of the thread to which the dye did not penetrate merely because of the overlying thread. Threads of cloth dyed in the aqueous sol are much more uniformly dyed even though the intensity of dyeing be less than that found on the surface of the cloths in the sols containing salts. In addition to this, in many cases the extra dye forced on by salt is lost on vigorous soaping in warm water so that the washed samples may show little effect of the presence of the salt while the unwashed samples show large differences. This is especially true of the liquefying salts at room temperature, and to a lesser extent of sodium sulphate, but it is not true of the cloths dyed in the hot solutions of either type of salts. Apparently in the hot solutions the penetration into the fibers is more complete and the adsorption more irreversible. There may be also some heat coagulation of the adsorbed dye. As was shown by Briggs for other substantive dyes, there is in the case of Congo red also an optimum concentration of salt: increasing concentrations up to this point produce increase dye adsorption by the cloth, while greater concentrations of salt produce decreased dyeing, the dye being flocculated within the solution instead of on the fiber. This agrees with the work of Auerbach[1] who showed that the best dyeing resulted from that concentration of dye which just produced turbidity in the dye solution during the hour of immersion.

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[1] Briggs: J. Phys. Chem., 28, 368 (1924).

Potassium iodide, which has such a well-known peptizing effect on gelatin was one of the first salts used and its effects are typical of the liquefying group of salts. In the absence of gelatin the first addition of potassium iodide (one gram in the 25 cc system) produced a marked increase in the amount of dye put on the cloth in one hour of immersion at room temperature. Two, three, or four grams of the salt gave about the same increased dyeing as shown by one gram; but, while the one gram sample showed only some turbidity, the remaining systems showed increasing coagulation and precipitation of the dye in the solutions during the hour at room temperature. Sols made as those just mentioned but containing five cc of the 2% gelatin in each all show less dyeing than the corresponding sols without gelatin and the difference produced by the first addition of potassium iodide is less than in the absence of the gelatin. The addition of the gelatin is sufficient to prevent the precipitation of any dye in the second set. In both series, soaping thoroughly in warm water removed practically all the excess dye forced on by the salt and while the soaped gelatin-sol dyed cloths are all lighter than the corresponding cloths dyed in the absence of gelatin, the soaped cloths in each series whose dyeing was aided by potassium iodide are of about the same shade as the blank (no salt) in each series.

The explanation of these phenomena is that potassium iodide destabilizes the Congo red making it more readily adsorbed on the surface of the cloth. The dye thus forced on is too coarse to have penetrated far or to be as strongly adsorbed as dye taken up in the absence of salt and is, therefore, less fast to washing. Obviously, the dye adsorbed on the surface will be more effective in making the cloth appear well dyed than that which has penetrated further but the latter which is adsorbed within the fiber will be better protected from removal by washing or rubbing. There is also seen the effect of the gelatin in being adsorbed on the surface and thereby covering it or portions of it so that the dye can not be there adsorbed and must diffuse through to and within the fiber. The potassium iodide therefore, has two effects. It tends to force the dye out of solution and in the absence of gelatin on to the cloth. It also tends to liquefy the gelatin or to send it into the solution phase as against its being adsorbed on the dye or on the cloth. The fact that the cloths dyed in the gelatin sols are all lighter and that the remaining solutions in that series are clear and without precipitated dye shows that the gelatin is not all peptized from the cloth but still exerts some blocking effect and that the destabilized dye is forced out not only on the cloth but also on the peptized gelatin which is still able to keep it suspended and to prevent its adsorption on the cloth.

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[1] Kolloid-Z., 30, 166 (1922).

Sodium iodide was found to have a similar effect to that shown by potassium iodide in dyeing from the gelatin-dye sols. A comparison was made between sodium iodide and sodium sulphate as these are representatives of the two classes of salts. This comparison shows that sodium iodide is more effective than the equivalent concentrations of sodium sulphate in forcing dye on cotton from gelatin-dye sols because the iodide tends to precipitate the dye but peptize the gelatin while the sulphate tends to precipitate both dye and gelatin on the cloth and thus accentuate the competition between them. Final systems were made up to contain 0.8 and 1.6 N NaI as well as 0.4, 0.8, and 1.6 N Na_2SO_4, each sol being also 0.4% gelatin and 0.04% Congo red. The cloths dyed in the presence of sodium iodide were darker (both original and washed samples) than any of those dyed in the presence of the sodium sulphate. The cloth dyed in the 0.4 N Na_2SO_4 system was the best in that set and was not much inferior to that dyed in the 0.8 N NaI, while the latter was markedly better than the cloth dyed in 0.8N Na_2SO_4. The 1.6 N Na_2SO_4 is distinctly beyond the optimum concentration, producing almost complete flocculation of the dye in solution and dyeing only a little better than the blank containing dye and gelatin only. Both the sodium iodide sols grew turbid during the hour while only the most concentrated sulphate sol did so. It appears, therefore, that the sodium sulphate tends rather to force the adsorption of the destabilized dye on the gelatin rather than on the cloth and that the dye-gelatin adsorption complex is not strongly adsorbed by the cloth for the washing carries off very little dye from the cloths dyed in the presence of the sodium sulphate. In other words the effect of the sodium sulphate is to decrease the dispersion and to increase the adsorptive power of both dye and gelatin for concentrations below that which causes coagulation. On the other hand the effect of the sodium iodide is to decrease the dispersion of the dye and cause it to become more adsorptive but at the same time the peptizing action on the gelatin is one of increasing dispersion and greater stability in the liquid phase and, therefore less adsorptive power. The result is that the Congo red micelles adsorb each other and precipitate instead of adsorbing gelatin and remaining suspended. This is shown by the fact that the sodium iodide samples (in common with those of the other liquefying salts at room temperature) lose considerable dye on washing. It is thus seen that a very important factor in the washing fastness of dyes is the size of the particles of dye on the cloth. The peptized gelatin being little adsorbed permits growth of the dye particles to such size that they are readily washed off, while the greater adsorptive power of the gelatin in the presence of sodium sulphate prevents the development of such large aggregates and the loss on washing is less. The difference here can not be ascribed to a difference in the amount of adsorption of the gelatin on the cloth which might then carry off dye with it on washing for in that case the sulphate samples should have more gelatin on the cloth and wash off worse; actually they wash off less than the iodide samples. Therefore, if this factor enters at all, it is secondary to the factor of particle size and adsorbability.

Conclusions

1. When sols of gelatin and of Congo red are mixed the two sols appear to continue to exist independently.

2. Gelatin adsorbs Congo red so slightly from solution as to render impossible any protection in the ordinary sense.

3. Congo red, in the absence of gelatin, behaves as a sol intermediate between the lyophile and the lyophobe types. It is precipitated by sodium and potassium halides and by various other salts.

4. In the presence of gelatin this precipitation by salts is greatly diminished or entirely prevented. This apparent protection by the gelatin is shown to be due to a decreased stability and decreased dispersion of the dye by virtue of which it is more strongly adsorbed by the gelatin.

5. Salts which liquefy gelatin and salts which precipitate gelatin have different effects on the dyeing of cotton cloth from the mixed sols of gelatin and Congo red.

6. Both types of salts increase the adsorption of dye from the mixed sols, the liquefying salts being more effective because of their action in peptizing the gelatin

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PHOTO-VOLTAIC EFFECTS IN GRIGNARD SOLUTIONS
II. NATURE OF THE EFFECTS

BY R. T. DUFFORD

Continuing the work described in a previous article,[1] dealing with photo-voltaic effects in cells containing anhydrous ether solutions of Grignard reagents, this paper reports the results of a later series of experiments made under considerably improved experimental conditions; the more important objects were to study the photo-voltaic responses of single electrodes, and to attempt to locate the seat of the effect, but incidental observations in several other directions were also possible, as will be noted later. While much more work is needed on both the questions suggested, sufficiently interesting results were obtained to seem to justify reporting the work, especially since the later extensions planned for the study have been greatly delayed. The results here reported are from observations on about thirty cells which were studied intensively, very long sets of readings being made in many cases. Most of the cells contained solutions of ethylmagnesium bromide or phenylmagnesium bromide, but four solutions not before reported as active are noted below.

While much the same apparatus was used as in the previous work, a number of important improvements were made, which added considerably to the reliability and the accuracy of the observations, and which therefore deserve mention. Experiments at the University of Missouri having shown the feasibility of using more intense illumination, the previous practice of illuminating with a 100-watt lamp was discontinued, and a special tubular-bulb 1000-watt lamp, such as is used for projection purposes, was used instead. The result was an enormous increase in the speed and amount of response of the cells, together with much greater freedom from ambiguity due to slow drift in voltage. For use in the "inner" thermostatic bath (described in the previous article), provision was made for removing the heat by surrounding the lamp with a water-jacket supplied with running water, the water being turned on and off nearly simultaneously with the lamp. Proper regulation of the water supply was obtained by using a gate-valve and stop-cock in series, the gate-valve being left set in the position found by preliminary trials to give the necessary rate of cooling. With this arrangement, the cells could be placed about three inches from the filament of the lamp, but immersed in water; they thus received an illumination comparable with that from noonday sunlight, though the small air bubbles that at times settled on the wall of the water-jacket reduced the illumination somewhat, so that no more precise statement of the value of the illumination would be justified. The temperature changes under this intense illumination were generally less than 1°C., and usually much less, since very long periods of illumination were no longer necessary; hence the temperature control was fully as good as in the previous work. A second 1000-watt lamp, used with the small bath, was not water-jacketed since it was outside the bath, usually at a distance, behind a lens. Figs. 1 and 2 give typical response curves obtained under these conditions; the improvement, compared with the curves in the previous article, is very plain. In the outer bath, the temperature could if necessary be held to .01°C. for hours at a time, owing to the use of cooling, good stirring, and a thermostat regulator of unusual sensitivity which was designed by Dr. E. Q. Adams, and will be described by him elsewhere.

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[1] Dufford: J. Phys. Chem., 34, 1544 (1930).

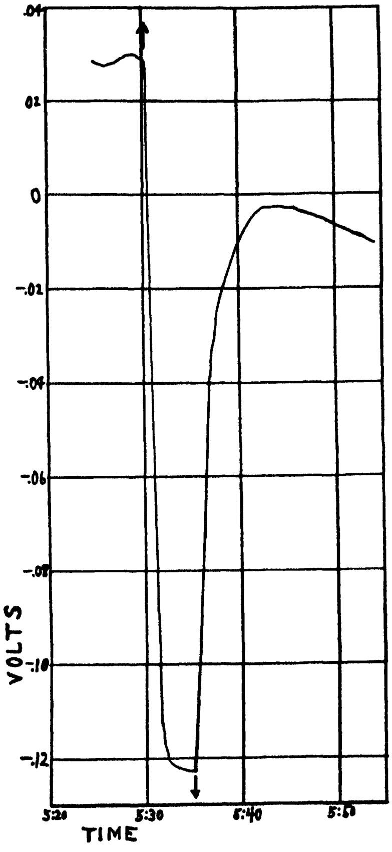

Fig. 1

Response (showing reversal of voltage) and recovery of a Pt/ΦMgBr/Al cell exposed to light from a 1000-watt incandescent bulb; cell was about four inches from filament. Both cell and lamp were immersed in water. Upward-pointing arrow indicates time light was turned on; downward-pointing arrow indicates when light was turned off.

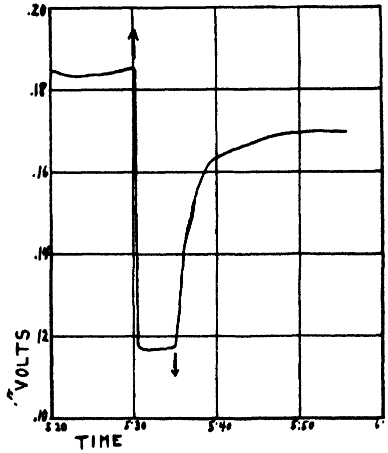

Fig. 2

Voltage response curve of a Pt/ΦMgBr/Al cell which had been depolarized with C_2H_5Br. The response is about half as large as in the similar un-depolarized cell shown in Fig. 1.

Further improvement resulted from the use of a more sensitive galvanometer than was available previously; a 500-ohm Type R instrument, sensitive to about 2 × 10^{-9} amps. per mm., with a universal shunt giving critical damping, was used, with about 0.5 megohm in series for all except the most feeble E. M. F.'s; hence the currents used in balancing were small enough not to produce troublesome polarization effects. In spite of the longer period of this galvanometer, readings could be obtained in 30 to 60 seconds; but because of the rapid changes resulting from the more intense illumination used, it was necessary to confine observations to one cell at a time. The same

Kohlrausch spiral was used as a potentiometer, but on an improved circuit, so that the potentiometer was direct-reading over either of the ranges 0–1 or 1–2 volts, giving twice the sensitivity previously used, and considerable increase in convenience; a switch made the old 0–2 volt range instantly available if needed. In addition, a quadrant electrometer was available for some time, through the courtesy of Dr. Henry Miller.

The ether used in making up the solutions was freshly redistilled over sodium, and was exceedingly dry and free from sodium. This precaution appears not to be entirely necessary, for in no case was any difference in behavior of a cell containing a Grignard solution found which could be attributed to the presence of sodium or its compounds dissolved in the ether. Apparently the same photo-voltaic behavior results if the ether is decanted after standing over sodium, although appreciable amounts of sodium will be dissolved. In order to avoid the presence of oxygen, the ether was distilled under nitrogen, and the compounds were prepared, and so far as possible were handled, under a nitrogen atmosphere. This refinement likewise produces little if any difference in the results. One cannot by this method be absolutely certain that every trace of oxygen has been excluded at every step of the preparation of a cell; and, on the other hand, a compound if properly handled need not be oxidized to any serious extent even if no nitrogen is used, the ether vapor serving the same purpose as the nitrogen, though less effectively, in displacing air.

A thorough set of tests was made on several cells to determine whether the potentiometer method of reading produced any polarization effect that would seriously affect the voltage of a cell. In these tests, the electrometer was left continuously connected to the cell, while the potentiometer was connected for readings and disconnected at intervals. One observer kept close record of the electrometer readings, while another read the potentiometer. On plotting the readings, the curve from the electrometer should show sharp breaks at the points where the potentiometer was connected in, if the voltage were disturbed; but instead, the electrometer curves were very smooth, like the potentiometer curves, on which they could be superposed; the effects due to polarization were less than the errors in reading the electrometer. While these observations are sufficient to give confidence in the potentiometer method of reading, they do not show that polarization effects are nonexistent. On the contrary, tests made on a Pt/ΦMgBr/Al cell showed that, if the cell were deliberately short-circuited for 20 seconds, the recovery curve was very similar to the recovery curve after illumination, with three-quarters of the original voltage recovered in the first ten minutes. The cell used had a "negative" E.M.F. (i.e. Pt negative) of about .083 volts, before being polarized, the value increasing to more than 0.2 on illumination for six minutes; the recovery was somewhat slower than from the polarization, but apparently tended to the same equilibrium value. Forcing a current through the cell in the opposite direction to its normal E.M.F. raised the voltage temporarily, with a quick initial recovery; shaking temporarily raised the voltage, and apparently reduced the equilibrium value slightly. Hence polarization effects exist and must be avoided. Phenyl compounds are much more easily affected by polarization than ethyl compounds, however.

The electrometer was able to settle one question which the potentiometer could not; it showed definitely the existence of a photo-voltaic effect with Pt-Al electrodes immersed in pure ether. The resistance of such a cell is too high to permit balancing a potentiometer. The first response is usually in the "positive" direction (Pt electrode more positive), but after two or three illuminations it becomes and remains negative. The absolutely pure ether showed a slightly larger response than ether containing sodium in solution, but the difference is probably not significant. Addition of a hydrocarbon halide, as phenyl bromide, increases the response, reversing it at once if it is not already negative. If iodine is also added, the response is much larger, and negative; but it sometimes shows the initial momentary throw in the wrong direction when the light is turned on or off. In one cell, some magnesium was also added, so that some phenylmagnesium bromide formed in the solution. This again doubled the response, which was still negative. Even the rapid oscillations of voltage occasionally observed elsewhere have been observed with the electrometer, thus showing them not to be due to polarization from currents during balancing. The effect in pure ether has been studied only with Pt-Al electrode combinations, and much remains to be done in investigating it. But the existence of the effect in pure ether seems to have some theoretical significance, as it appears to rule out certain types of explanations of the effect. This point will be referred to in a later article.

In the preceding paper, it was noted that the initial rate of change of voltage of an illuminated cell was approximately a linear function of the intensity of the illumination. With the increased illumination available, which carried with it the possibility of reaching a definite end-point, much more free from the uncertainties due to voltage drift than readings lasting for longer intervals of time, it was possible to extend the study of intensity effects a step, and test how the end-point depended on the illumination. A long series of readings was made on two Pt/ΦMgBr/Al cells, one of which was a depolarized cell (the method of depolarizing will be explained below). The end-voltages, or rather the end values of the response, of course increase with the illumination, but apparently not according to any simple law. The curves are approximately logarithmic in form, but with some of the points corresponding to low illuminations somewhat uncertain. The un-depolarized cell was much more sensitive, and gave a more nearly straight line when the logarithm of the illumination was plotted against the response.

Several temperature tests served to confirm the conclusions stated in the previous article, that the temperature effects in those cells are small compared with the photovoltaic effects. Temperature changes can rarely account for as much as ten percent of the observed change in voltage in an illuminated cell. It was found further that the sensitivity of a cell does not vary rapidly with the temperature; cells in ice-water gave practically the same response as cells in water at 25° C.

With the increased illumination, tests could be made to compare the effects of different wave-lengths of light, under much more satisfactory conditions than before. Using monochromatic filters, tests on ten cells confirmed the earlier conclusion that the sensitivity extends from the deep red to the near ultraviolet, at least; but with smaller responses at the red end of the spectrum than at the violet. No cases were found where the responses were different in direction for different wave-lengths. The sensitivity curve for such a cell appears to be flatter than that for a human eye, and broader, and with the maximum at somewhat shorter wave-lengths.

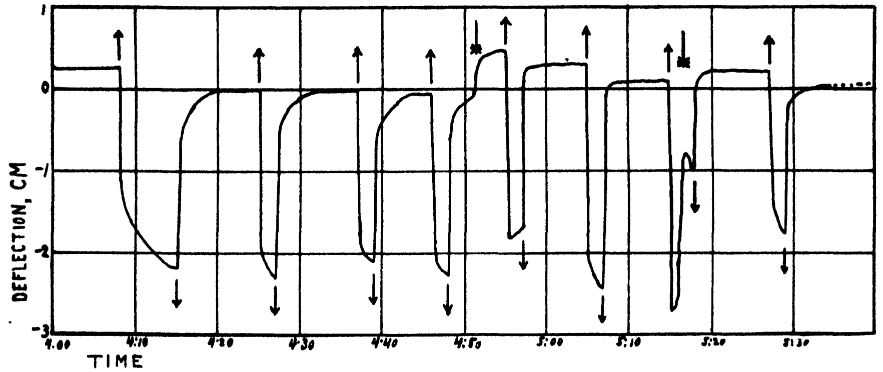

FIG. 3

Current response curve from a Pt/ΦMgBr/Al cell on closed circuit, under same conditions of illumination as in Figs. 1 and 2. Shaking (indicated by astericks) produced a temporary shift in the value of the dark-current. 1 cm. deflection corresponds to 1.78 x 10^{-8} amperes.

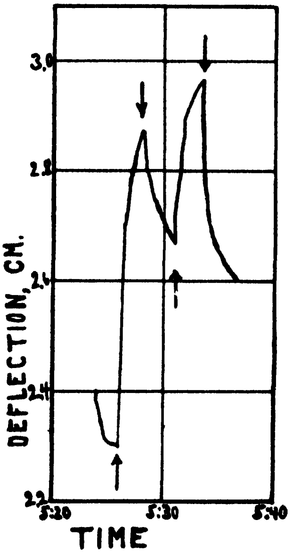

FIG. 4

Current response curve from a Pt/ΦMgBr/Al cell depolarized with C_2H_5Br. 1 cm. deflection corresponds to 1.78 × 10^{-6} ampere. The currents in this test are more than 100 times as large as in the test shown in Fig. 3.

A most interesting method of using cells of this type, is to put them on closed circuit, using the galvanometer as a current-measuring instrument, rather than as a null instrument as with the potentiometer. The voltage is of course not the same as it would be on open circuit. But the current settles down to a very small steady value, usually giving from 1 to 3 mm. deflection on the galvanometer, in a very short time. In most cases, the value of this current is not visibly affected by removing the half-megohm resistance kept in series with the galvanometer; hence the cells have enormous resistances, which appear to be due largely to polarization. Under these conditions, illuminating the cell will increase the current till the deflection is several centimeters, and occasionally so much that it is necessary to use a lower range on the universal shunt. Frequently this response current is in the opposite direction to the small residual current. The response reaches its end-value very quickly, and the recovery is equally rapid. Some typical response curves are shown in Figs. 3 and 4. It will be seen that successive illuminations give much more similar responses than are often obtained on open circuit. While this method of observation probably does not give accurate information concerning the voltage changes on illumination, it does give promise of being an extremely useful method of using such cells. Long life could hardly be expected of a cell on closed circuit; long-time tests were not made, but cells left on closed circuit overnight were still active. The currents observed were too small to read on a coarse instrument like a milliammeter; but no doubt larger currents could be obtained by using larger electrodes.

The writer is indebted to Dr. Wallace H. Carothers for the information that these cells can be depolarized by the addition of such substances as ethyl bromide, methyl iodide, or benzyl chloride. While it has not been possible to make an attack on the question as to why the effect occurs (work in this direction is now being started), it is remarkable how large an effect is produced. The addition of three to five cc. of ethyl bromide to a cell will produce a great increase in the current, sometimes several hundred-fold; and the voltage is also generally increased. The usual rule is that the response to light is decreased somewhat, but not completely destroyed. Good responses are still obtainable on either closed or open circuit. Comparison of Figs. 1 and 2, and of Figs. 3 and 4, will show the nature of the effect.

In order to make a beginning at the problem of locating the seat of the effect, arrangements were made for illuminating only one electrode at a time; the observations would thus show whether one or both electrodes were involved. For this purpose, cells were made in the shape of a H, by connecting a pair of 1-inch test-tubes by a small cross-tube. The H was filled to a height above the cross-tube, the electrodes were pushed well down to near the bottom of the side tubes, and the whole cell was wrapped in black friction-tape except for the region around one electrode. The amount of light that was scattered up to and through the cross-tube and down to the other electrode was very small. The tests so far made have disclosed a photovoltaic response with every electrode used; tests were made with both ethylmagnesium bromide and phenylmagnesium bromide solutions. With phenylmagnesium bromide cells, all the metals studied (Mg, Al, Cu, Zn, Pb, Fe) except platinum gave positive responses, i.e., became more positive with respect to the un-illuminated electrode, when exposed to light. The behavior of platinum, which it was expected would have the most uniform response, proved to be very puzzling, the response being sometimes positive and sometimes negative. The positive responses usually occurred with freshly inserted electrodes, the response usually becoming negative on standing. In the ethylmagnesium bromide cells, the results were similar, but the platinum gave a consistently negative response. It therefore follows, as had been suspected from earlier tests, that the effect in cells with one electrode platinum and the other of a base metal is the sum of the effects from the two electrodes. Also the platinum is shown to be responsible at least in part for the inconsistent behavior often observed in such cells.

Many experiments were made in an effort to learn more concerning the reason for the behavior of the platinum. It was thought that the effects might be associated with films formed on the surface of the platinum electrodes. There is much evidence for the existence of such films, not only from the phenomena of galvano-luminescence,[3] but also from work done by the writer's colleague, Dr. H. E. Hammond,[4] since the present work was finished. The latter work has shown the existence of very large capacitances, larger than a microfarad per square centimeter of electrode surface, between the electrodes and the electrolyte, in cells of the present type; it seems necessary to infer from these results, the existence of films of approximately monomolecular thickness. But these films do not seem to be associated with the photovoltaic effect, nor is it certain, perhaps not even probable, that these thin films are responsible for the galvano-luminescence. But in some preliminary experiments at the University of Missouri, it had been found that a platinum electrode which was coated with either oxidation product or hydrolysis products from a phenylmagnesium bromide solution, and then reinserted in the solution, would take on an unusually high positive potential with respect to the other electrode, and would increase that voltage when illuminated. It might be inferred that the positive response is due to a coating containing oxygen, or oxidation products. Similarly, aluminum electrodes seem to give a somewhat better response if left coated with oxide, just as cut from the sheet, than if carefully cleaned by sandpapering. On this view, the gradual change of the response of the platinum from positive to negative would be due to the loss of a film of oxide, rather than to the formation of a film. On this view, other metals than platinum might possibly give a negative response if they could be put into a condition sufficiently free from oxygen. If this prediction is true, it remains to be verified.

The available evidence is partly for, partly against such a view. Two kinds of experiments seem to support it. If the response is due to changes in a film, changes produced by other than photochemical processes should also cause a similar response. The sensitiveness of certain cells to mechanical disturbance was noted in the preceding article of this series; possibly it may be explained in this way. Tests were made to see if a similar result would be produced by deliberate scraping of the electrode surfaces by a glass scraper introduced through a small hole in the stopper, in the same way that the rectifying film on a Al electrode in a Nodon valve can be punctured. The results were somewhat erratic and unconvincing, but seemed best explained by assuming that the scraping tool brought a fresh supply of oxygen-containing material with it. A second bit of evidence came with the discovery that in Pt-Al cells old enough to have developed the normal negative response, the direction of the response could be reversed by shaking or by bubbling air through the solution a short time. But the response curve after this sort of reversal has a somewhat different shape than usual; the response is weak, and soon dies out under continued illumination. This response may therefore be due to a different process.

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[3] Dufford: J. Opt. Soc. America, 18, 17 (1929). Further work is in preparation for publication.

[4] Hammond: Phys. Rev. (2), 35, 998 (1930).

If the positive response is due to oxygen, apparently it should be possible to prepare platinum electrodes so free from oxygen that they would give a negative response immediately. Attempts were made to prepare such electrodes by outgassing platinum electrodes by heating in a hydrogen atmosphere at about 800°C. for several hours, allowing them to cool in hydrogen, and to remain in hydrogen until used. No difference in behavior was found between these electrodes and those used after cleaning and heating in a flame. An electrode kept for several days between freshly cut surfaces of sodium metal in ether, and transferred quickly to its cell, showed similar behavior. It is hard to see how these electrodes could have had much occluded oxygen. Hence if the initial positive response is due to an oxygen-carrying film, the film probably gets coated on the electrode when the latter is inserted in the solution.

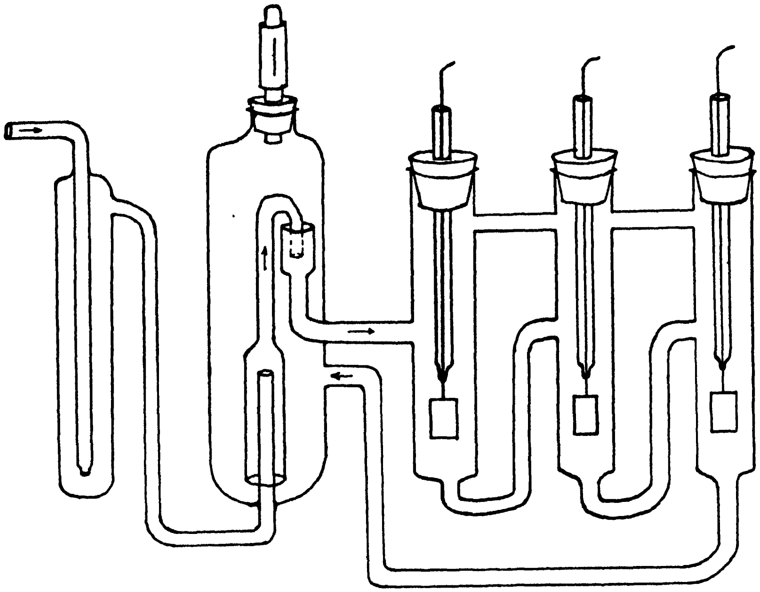

FIG. 5

Circulator used in studying effect of light on electrolytes of photo-voltaic cells.

Experiments of another sort, however, show conclusively that a photovoltaic effect due to a polarization film cannot possibly be all that exists. To test whether the electrolyte itself is affected by the illumination, a device was constructed which would permit the solution to be circulated, the illuminated electrolyte being carried to an electrode which had been kept in the dark. The experiment was suggested by the work of Lifschitz and Hooghoudt[5] which appeared while the present work was in progress; but the ease with which Grignard compounds unite with oxygen makes the problem of circulating them more difficult than if they could be permitted to come into contact with air. The writer makes grateful acknowledgment to Dr. E. Q. Adams for valuable suggestions regarding the design of the circulator used. As shown in Fig. 5, nitrogen from a tank was purified from traces of oxygen and saturated

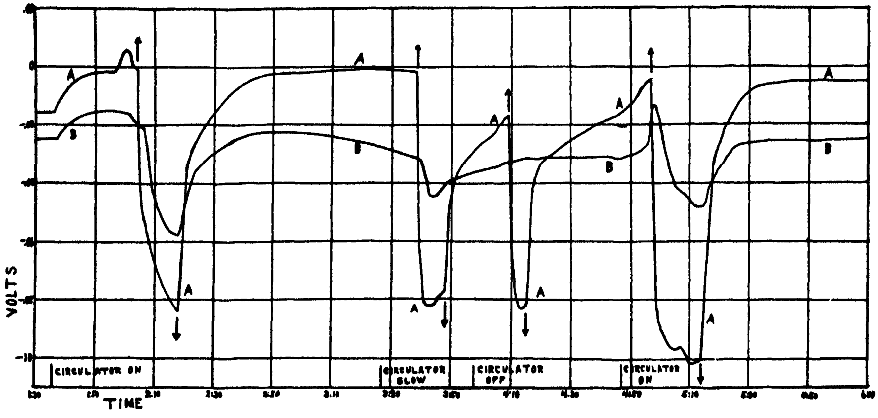

FIG. 6

Curves obtained with circulator shown in Fig. 5. Curve A records the difference of potential between the middle (illuminated) electrode and the upstream electrode; B, the P.D. between the downstream electrode (not illuminated) and the reference electrode. Pt electrodes and C_2H_5MgBr solution were used. The curves show that the solution carried with it an effect which altered the potential of the downstream electrode, but that the alteration became smaller or zero as the circulation was slower or completely stopped.

with ether vapor by bubbling through a separate lot of Grignard solution; it then bubbled through the nitrogen-lift in the reservoir, carrying with it the solution to be circulated, and finally escaped through a Bunsen valve. The solution pumped into the hopper in the reservoir by the nitrogen, passed through the three test-tubes sealed together, and finally returned to the reservoir. Each tube contained a platinum electrode. It was found that the circulation of the solution did not disturb the electrode potentials seriously. Only the middle electrode was illuminated; the electrode upstream from the others served as a reference electrode, and a record was kept of the differences of potential between this electrode and the two downstream from it. With the solution at rest, illuminating the middle electrode did not effect the potential of the electrode downstream from it. With phenylmagnesium bromide solution, circulating the solution seemed to carry a weak effect, reducing the potential of the third electrode, though the response of the middle electrode was positive. The tests were less satisfactory than might be desired; the response of the third electrode was small. But with ethylmagnesium bromide, the effect was unmistakable; the solution clearly carried with it something that reduced the potential of the electrode downstream. Fig. 6 shows the type of curve obtained. The effect was the same when the middle electrode was pulled up out of the solution, so that only the electrolyte was illuminated.

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[5] Lifschitz and Hooghoudt: Z. physik. Chem., 128, 87 (1927), and later articles. The complete references cited in their articles have made it seem unnecessary to give a complete bibliography here.

These experiments seem to indicate that more than one photo-voltaic effect is present; first, an effect carried by the electrolyte, which lowers the potential of a platinum electrode; and second, at least in phenlymagnesium bromide solutions, an effect which raises the potential of a platinum electrode, and is not carried by the solution; this effect may possibly be associated with surface films on the electrodes. The effect noted on introducing oxygen, which gives a somewhat different positive response, may prove to be a third kind of effect. The experiments have not been extended so that the responses of other metals than platinum can be classified. But work in this direction is being started again, and the writer hopes to communicate the results in a later paper.

In the course of the present work, four compounds not previously tested were investigated. An attempt was made to obtain a Grignard compound from ethylene bromide (dibromoethane). The reaction proceeds vigorously, yielding a solution which strongly resembles a Grignard solution, having a brownish color, forming a double layer if sufficiently concentrated, reacting vigorously with water, etc. But the solution is entirely non-luminescent on oxidation (it shows galvano-luminescence, however), and later work at the University of Missouri has shown that a practically quantitative yield of etherated magnesium bromide, usually assumed to be $MgBr_2.2(C_2H_5)_2O$, is obtained. Both layers of this solution give a strong photovoltaic effect. The other compounds studied were the Grignard reagents obtained from ortho-, meta-, and para-bromotoluene. The curves from these compounds (using Pt-Al electrodes) were obtained by electrometer. The para compound gave the largest response, the ortho nearly as large, and the meta compound the least. The order is the same as the order of brightness in the oxy-luminescence of these substances. Study of similar isomeric series of compounds would be desirable; evidently the effect of the position of benzine-ring substituents affects photovoltaic phenomena in a way analogous to the effect on chemiluminescence.

Summary

1. Additional observations, made under considerably improved experimental conditions, are reported, which give further information on the Becquerel effect in cells containing ether solutions of Grignard reagents. Earlier conclusions regarding temperature and wave-length effects are confirmed.

2. Comparisons of electrometer and potentiometer readings show that the potentiometer method of observing, properly handled, is entirely reliable, and not responsible for effects that might have been thought due to polarization while balancing.

3. The voltage response is found to be roughly proportional to the logarithm of the illumination.
4. The existence of an effect in pure ether is shown.
5. The current response of such cells on closed circuit is described.
6. Preliminary study is made of the remarkable increase of current obtainable when certain substances are used as depolarizers. The photovoltaic response is reduced but not destroyed by the depolarizers.
7. The direction of the voltage response of several metals, when single electrodes are illuminated, is noted.
8. Evidence is adduced to show that at least two types of response may occur with platinum electrodes.
9. Four additional compounds are noted to show the effect.

The work described above was done at the Research Laboratory, Incandescent Lamp Department of General Electric Co., Nela Park, Cleveland, Ohio. The writer takes pleasure in expressing his gratitude to Director W. E. Forsythe and to the other members of the staff, who made it possible to carry out the work under unusually pleasant circumstances.

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THE DEGREE OF DISSOCIATION AND THE IONS OF CADMIUM IODIDE IN AQUEOUS SOLUTION

BY JAMES W. McBAIN, PIERRE J. VAN RYSSELBERGE AND W. A. SQUANCE*

During electrolysis of all stronger solutions of cadmium iodide the cadmium moves away from the cathode instead of toward it.[1] Hittorf gave the only possible explanation; namely, that more cadmium is moving in complex anions towards the anode than is traveling in the form of cations toward the cathode. The other properties of these solutions are in accordance with this behavior which seems to be coupled with very incomplete dissociation of the molecules into ions. Thus the lowering of the freezing point is deficient and the concentration of ions as given by measurements of E.M.F. and conductivity is much less than that exhibited by corresponding salts of magnesium or calcium. However, the difference, as will appear, is one of degree only, and a careful scrutiny of the data for cadmium salts is therefore of general significance in the search for a valid hypothesis of electrolytic dissociation. We present in this paper a discussion of the data, including a new general method for the calculation of the concentrations of the different ionic species present, based upon migration numbers and E.M.F., and independent of the theory of activity coefficients. The results so obtained are used in the discussion of new diffusion data for cadmium iodide.

In Fig. 1 all the available data for the observed transference of cadmium in solutions of four cadmium salts have been plotted against the logarithm of the concentration.[2] The curves indicate that the migration number is nearly constant from infinite dilution up to a certain low concentration, 0.01 molar in the case of cadmium iodide and 0.056 and 0.11 molar for cadmium bromide and chloride, respectively. For higher concentrations the curves drop rapidly, and the total movement of cadmium is zero in 0.23 molar cadmium iodide, thereafter becoming negative and seeming to tend toward a limit of −0.23. A negative value for the transference number of cadmium in cadmium bromide has been obtained by Gordon (loc. cit.) with a solution containing 29.4 per cent cadmium bromide. In the case of cadmium chloride, a negative value has been obtained by Hittorf (loc. cit.) (1902, 1903) for a concentration of 7.69 gram mols per liter. The similarity between the curves for the three halides is striking; they are almost parallel, a fact which shows that the three salts dissociate in the same manner and form complexes of the same types at high concentrations.[1] For cadmium iodide the complex anion is almost certainly CdI_3^-.

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* Died in 1922.

[1] W. Hittorf: Pogg. Ann., **106**, 543 (1859); Z. physik. Chem., **39**, 613 (1902); **43**, 239 (1903); J. W. McBain: Z. Elektrochemie, **11**, 215 (1905); monograph, Proc. Wash. Acad. Sci., (A compilation of the experimental data of the quantitative measurements of electrolytic migration), **9**, 1 (1907); B. Redlich: Z. physik. Chem., **37**, 673 (1901); **38**, 127 (1901); V. Gordon: Z. physik. Chem., **23**, 469 (1897).

[2] See McBain's monograph (loc. cit) and G. Heym: Ann. Physique, **12**, 443 (1919) (the concentrations had to be recalculated); W. W. Lucasse: J. Am. Chem Soc., **51**, 2597 (1929) (results for $CdBr_2$ were not plotted because they coincide with those of the other authors).

Similar negative values for the transference number have been obtained for $ZnCl_2$[2], ZnI_2[3] and $CuCl_2$[4]. Movement toward the anode of complex ions containing cobalt has been detected but not measured in mixtures of $CoCl_2$ with concentrated HCl, $MgCl_2$ and $CaCl_2$[4]; complex ions containing iron, copper, move toward the anode in mixtures of $FeCl_3$ and $CuCl_2$ with concentrated HCl[4]. The same result has been obtained in mixtures of $CuCl_2$ with $MgCl_2$, $CaCl_2$, LiCl.[5] Complex anions containing Cu, Fe and UO_2 have been detected in mixtures of $CuSO_4$, ferric and uranyl salts with alkali bicarbonate in excess.[6] Rieger found complex ions in some mixtures; in a solution of potassium ferrous oxalate he found the iron migrating toward the anode.[7]

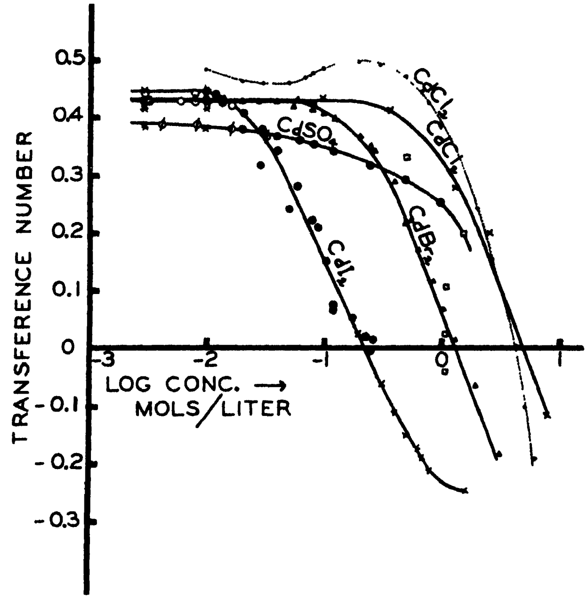

Fig. 1

Transference of cadmium in solutions of four cadmium salts. Hittorf, ×; Goldlust, ϕ; Bukschewski, o; Goldhaber, △; Kummel, *; Gordon, □; Heym, ⊗; Redlich, ●; Lucasse, --●--

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[1] F. Bourion and E. Rouyer (Ann. Chim, (10), **10**, 182 (1928); Compt. rend., **184**, 598 (1927)) found from ebullioscopic studies of salt pairs that cadmium chloride forms complexes with potassium, sodium and ammonium chlorides just as did cadmium iodide with potassium iodide. See also E. Rouyer: Ann. Chim., (10), **13**, 423 (1930); F. Bourion and O. Hun: Compt. rend., **191**, 97 (1930).

[2] W. Hittorf: loc. cit.

[3] W. Hittorf: loc. cit. (1859).

[4] V. Kohlschutter: Ber. **37**, 1, 1153 (1904).

[5] F. G. Donnan and H. Bassett: J. Chem. Soc., **81**, 939 (1902).

[6] R. Luther and B. Krsnjavi: Z. anorg. Chem., **46**, 170 (1905).

[7] E. Rieger: Z. Elektrochemie, **7**, 863, 871 (1901).

A survey of migration data therefore shows that cadmium iodide is not the only salt of its kind. For almost all the strong electrolytes, the transference number of the slower ion decreases rapidly at high concentrations; negative values are not generally obtained because the solubilities are rarely large enough.

Having admitted complex anions to explain the negative parts of the curves, we have also to admit that such anions are present in more dilute solutions of these salts. For example, in the case of cadmium iodide they are present in sufficient amount appreciably to affect the transport number in all solutions down to 0.01 molar.

The change of transference number with change in concentration in solutions of strong electrolytes has often been interpreted as signifying unequal changes in the mobilities of the ions.[1] This explanation cannot account for negative values, although it is the only one permissible in theories of 100 per cent dissociation. The data just adduced show that cadmium iodide is by no means to be regarded as a unique exception but rather as merely an extreme case.

In previous communications we have shown[2] that negative transport numbers may be obtained for dilute solutions of any salt involving any divalent ion, provided that a sufficient addition of common anion be made to the solution. This is just like the behavior of cadmium iodide to which a solution of potassium iodide has been added.[3] The interpretation of the data for cadmium iodide, therefore, becomes of direct significance for all other solutions.

McBain in 1905 (loc. cit.) explained quantitatively the properties of solutions of cadmium iodide then known by assuming very incomplete dissociation and the presence of the complex anion CdI_3^- and the partially dissociated cation CdI^+. The three dissociations occurring were then

$$CdI_2 = Cd^{++} + 2I^-$$
$$CdI_2 = CdI^+ + I^-$$
$$3CdI_2 = Cd^{++} + 2CdI_3^-.$$

A complex ion of the type CdI_4^{--}, as originally suggested by Hittorf[4], was regarded as improbable, because it is very unlikely that this ion would possess a migration velocity several times greater than the simple Cd^{++} and I^- ions. As a matter of fact it is possible that many types of complexes are present together, but by assuming the existence of one or two definite ones, in some cases reasonable explanations can be obtained for most of the properties of the salt.

Van Name and Brown[5] in 1917 accepted these ions but rejected the calculated concentrations for three reasons. The first was a misunderstanding, whereby, through confusing equivalent and molar conductivity, they thought that the calculated conductivity was only half that observed. The second was because they assumed that simple molecules must freely combine with iodine, whereas they felt that they need not make such an assumption if they assumed double molecules of cadmium iodide. The third reason was that they inferred from E.M.F. data, using an iodine electrode extrapolated to solutions containing no iodine, that the concentration of the I^- ion in such solutions was higher than that calculated by McBain. Actually, for the same reason as indicated above, McBain's value is somewhat higher than theirs. His was for a decimolar solution $0.126 \times 0.2 = 0.0252$ N I^- as compared with their value 0.021 N I^-.

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[1] See, for example, G. Jones and M. Dole: J. Am. Chem. Soc., **51**, 1073 (1929).

[2] J. W. McBain and P. J. Van Rysselberge: J. Am. Chem. Soc., **50**, 3009 (1928); **52** 2336 (1930).

[3] W. Hittorf: Ostwald's Klassiker, **23**, 87; J. W. McBain: loc. cit. (1905).

[4] For a revision of Hittorf's calculation of his data see McBain: loc. cit. (1905).

[5] R. G. Van Name and W. G. Brown: Am. J. Sci., **44**, 453 (1917).

The present paper is divided into two parts. In the first are recorded electromotive force measurements carried out by one of us (W. A. S.) at the University of Bristol in 1922. They are used, together with other electromotive force data obtained by Getman[1] and with migration data, in the calculation of the concentrations of the various ionic species present in aqueous solutions of cadmium iodide. In the second part, diffusion data obtained by Dr. Tsun Hsien Liu at Stanford in 1930 are presented and discussed in the light of the information obtained in Part I as to the composition of aqueous solutions of cadmium iodide.

PART I

Experimental

Measurements were made of the E.M.F. of the following cells together with two in which KI was added to the CdI_2:

Cd	CdI_2 0.001– 0.4 M	KCl satd.	KCl, Hg_2Cl_2 0.1 N solid	Hg

Hg	Hg_2I_2, solid	KI 0.1 and 0.05 M	KCl satd.	KCl, Hg_2Cl_2 0.1 N solid	Hg

Hg	Hg_2I_2, solid	CdI_2 0.1 M	KCl satd.	KCl, Hg_2Cl_2 0.1 N solid	Hg

Merck's pure cadmium was fused to a stout copper wire without solder and the copper, including about 1 cm. of the cadmium beyond the joint, was sealed into a glass tube with shellac, sealing wax or piccin. Other materials were Kahlbaum's purest chemicals. The Weston cadmium cell was standardized by the National Physical Laboratory. Decinormal calomel electrodes were made and used in duplicate. It was assumed that the saturated KCl had eliminated diffusion potential. All vessels and instruments used were calibrated. A large Kohler precision potentiometer was employed together with a delicate Leeds and Northrup ballistic galvanometer.

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[1] F. H. Getman: J. Phys. Chem., 32, 941 (1928).

After each series of measurements on a solution of one concentration, the cell was taken apart and the cadmium electrode washed and then rubbed with a fresh piece of emery cloth to ensure removal of any oxide or other contamination. It was found impractible to use a dilute solution of ammonia to remove the oxide film, as suggested by Richards, except when piccin was used instead of shellac for insulating material, because on standing the ammonia attacked the shellac. The cadmium electrodes were tested immediately before use, and a potential difference of ±0.0002 volt was considered sufficiently small to proceed with the actual measurement of the electromotive force of the combination cell employing one of these electrodes.

The electromotive forces given in Table I are the means of a series of observations and in several cases represent the average of two or more entirely independent series made upon solutions of the same concentration. The negative sign indicates that the named electrode was negative as compared with the mercury of the calomel electrode. The concentrations are expressed as mols per liter, and the values for the electromotive force are considered accurate at room temperature to within ±0.002 volt.

TABLE I

E.M.F. of Cells at 20° consisting of Solutions of Cadmium Iodide and Potassium Iodide, alone and together, measured against N/10 Calomel Electrodes through Saturated Solutions of KCl

Electrode	Concentration of salt Mols per liter	E. M. F. Volts
Cd/CdI_2	0.001	−0.8133
"	0.01	−0.8061
"	0.05	−0 8028
"	0.1	−0.7958
"	0.2	−0.7896
"	0.3	−0.7808
"	0.4	−0 7718
Hg/Hg_2I_2, KI	0.05	−0.2927
"	0.1	−0 3094
Hg/Hg_2I_2, CdI_2	0.1	−0.2799
Hg/Hg_2I_2, K_2CdI_4	0.025	−0.2916
Cd/K_2CdI_4	0.025	−0 8238

A. Mobilities of the Simple and Complex Ions.

We shall suppose that the mobilities of the simple ions Cd^{++} and I^- vary with concentration but remain proportional to their values at infinite dilution. For CdI_2 the transference numbers of Cd^{++} and I^- at infinite dilution are, respectively, 0.45 and 0.55. Our assumption on the mobilities means that, at any concentration, the ratio of the mobilities of the Cd^{++} and I^- ions is equal to 0.45/0.55.

The mobility of the ion CdI_3^- was calculated by McBain (loc. cit. 1905) who used two different methods. The first one is based upon migration data for pure CdI_2 in concentrated solutions; the second is based upon a recalculation of Hittorf's experimental data for migration in the mixture $2KI + CdI_2$. If we assume that in very concentrated solutions we have only Cd^{++} and CdI_3^- ions, a hypothesis corroborated by E.M.F. data, the transference number of CdI_3^-, or better the ratio of its mobility to the sum of the mobilities of Cd^{++} and CdI_3^-, is given by $1.23/3 = 0.41$. This value 0.41 means that the complex ions CdI_3^- carry 41 per cent of the total current carried by the ions resulting from the dissociation

$$3CdI_2 = Cd^{++} + 2CdI_3^-$$

or that the mobilities of Cd^{++} and CdI_3^- are in the ratio of 0.59 to 0.41.

McBain had to assume that the CdI^+ ion had the same mobility as the Cd^{++} ion, because no data were available for the calculation of its exact value. In part B, we shall show that this mobility can be deduced from E.M.F. data. The calculation gives the ratio between the mobilities of CdI^+ and I^- equal to $0.16/0.55$.

B. Evaluation of the Data for E.M.F.

In the first type of cell used in Table I the E.M.F. depends solely upon the concentration of Cd^{++} ions, and for any two concentrations the difference in E.M.F. observed is

$$E_1 - E_2 = 0.029 \log \frac{(Cd^{++})_2}{(Cd^{++})_1}$$

where changes in activity coefficient are neglected.

Getman[1] has recently measured cells of the type Cd | CdI_2, AgI | Ag, and for any two concentrations the difference in E.M.F. observed is

$$e_1 - e_2 = 0.029 \log \frac{(Cd^{++})_2(I^-)_2^2}{(Cd^{++})_1(I^-)_1^2}$$

Hence

$$e_1 - e_2 - E_1 + E_2 = 0.058 \log \frac{(I^-)_2}{(I^-)_1}$$

Thus the two series of data, considered together, furnish the ratios of Cd^{++} ions as well as I^- ions in the two solutions.

To obtain absolute amounts, we have assumed that the concentrations of Cd^{++} ion and I^- ion in 0.005 molar CdI_2 are given by conductivity. It was shown in McBain's paper (loc. cit. 1905) that for low concentrations the data for freezing point and conductivity are in close agreement, and similar freezing point data were since obtained by Van Name and Brown (loc. cit.). Hence we take the concentrations in 0.005 molar CdI_2 as 0.00315 molar Cd^{++} and 0.0063 I^-, the degree of dissociation being 63 per cent.

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[1] F. H. Getman: J. Phys. Chem., 32, 941 (1928).

In Table II the calculation of the concentrations of the cadmium and iodine ions relative to their concentrations in a 0.005 molar CdI_2 solution are given, using smoothed values for both Squance's and Getman's curves for E.M.F. and converting Getman's concentrations into mols per liter by means of the densities given in International Critical Tables.

TABLE II

Concentrations in Mols per Liter of Iodine and Cadmium Ions deduced from E.M.F. Data of Squance and Getman and the Degrees of Dissociation of the Two Ions.

Total cadmium	$-e_2$ volts	$-E_2$ volts	(I^-)	(Cd^{++})	$\frac{\frac{1}{2}(I^-)}{(CdI_2)}$	$\frac{(Cd^{++})}{(CdI_2)}$
0.005	0.6078	0.8082	0.0063	0.00315	0.630	0.630
0.01	0.5933	0.8061	0.0103	0.0037	0.515	0.370
0.02	0.5701	0.8050	0.0148	0.0040	0.370	0.200
0.05	0.5605	0.8028	0.0228	0.0048	0.228	0.096
0.1	0.5512	0.7958	0.0252*	0.0084	0.126*	0.084
0.2	0.5380	0.7896	0.0285	0.0138	0.071	0.069
0.5	0.5285	0.765	0.0181	0.0973	0.018	0.194

* The same fraction was obtained from the freezing point data by McBain in 1905, but ignoring any CdI^+ present (loc. cit., compare page 1001 above).

C. Migration Data applied to the Calculation of the Concentrations of Complex Ions.

1. Calculation of the mobility of the CdI^+ ion.

Let us suppose (see Fig. 1) that for a concentration of 0.01 mol/l. the concentration of the CdI_3^- complex is 0. Then the apparent transference number of the Cd^{++} ion is given by the general expression[1]

$$N_{Cd} = \frac{2(Cd^{++}) \cdot \frac{m_{Cd}}{m_I} + 2(CdI^+) \cdot \frac{m_{CdI}}{m_I} - 2(CdI_3^-) \cdot \frac{m_{CdI_3}}{M_I}}{2(Cd^{++}) \cdot \frac{m_{Cd}}{m_I} + (CdI^+) \cdot \frac{m_{CdI}}{m_I} + (I^-) + (CdI_3^-) \cdot \frac{m_{CdI_3}}{m_I}}$$

where the m's represent the respective mobilities referred to any common unit. For the concentration 0.01 mol/l. we have

$$N_{Cd} = \frac{2(Cd^{++})\frac{0.45}{0.55} + 2(CdI^+)\frac{m_{CdI}}{0.55}}{2(Cd^{++})\frac{0.45}{0.55} + (CdI^+)\frac{m_{CdI}}{0.55} + (I^-)} = 0.45$$

E.M.F. data gave:

$$(Cd^{++}) = 0.0037$$
$$(I^-) = 0.0103$$

As $(CdI_3^-) = 0$,

$$(CdI^+) = (I^-) - 2(Cd^{++}) = 0.0029$$

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[1] Miss M. E. Laing: J. Phys. Chem., **28**, 673 (1924).

Hence the equation when solved for m_{CdI} gives:

$$m_{CdI^+} = 0.16,$$

expressed in the same units as give $m_{I^-} = 0.55$. That is, the equivalent conductivity of CdI^+ is 0.16/0.55. or 29 % of that of the I^- ion.

2. Calculation of (CdI_3^-) *as a function of* (Cd^{++}), (I^-) *and* N_{Cd}.

In the same way,

$$N_{Cd} = \frac{2(Cd^{++}) \cdot \frac{0.45}{0.55} - 2(CdI_3^-) \cdot \frac{0.41}{0.59} \cdot \frac{0.45}{0.55} + 2(CdI^+) \cdot \frac{0.16}{0.55}}{2(Cd^{++}) \cdot \frac{0.45}{0.55} + (CdI_3^-) \cdot \frac{0.41}{0.59} \cdot \frac{0.45}{0.55} + (CdI^+) \cdot \frac{0.16}{0.55} + (I^-)}$$

Replacing (CdI^+) by $(I^-) + (CdI_3^+) - 2(Cd^{++})$ and solving for (CdI_3^-) we obtain:

$$(CdI_3^-) = \frac{(0.26 - 0.58\, N_{Cd})\,(Cd^{++}) + (0.32 - 0.71\, N_{Cd})\,(I^-)}{0.4727\, N_{Cd} + 0.3054}$$

It is easily seen that, when $N_{Cd} = 0.45$ (corresponding to the migration number for extreme dilution), $(CdI_3^-) = 0$. Again, the equation is reduced to an identity when N_{Cd} is put equal to -0.23, (I^-) equal to 0 and (CdI_3^-) equal to 2 (Cd^{++}). Knowing the values of N_{Cd}, (Cd^{++}) and $I(^-)$, it is then possible to calculate (CdI_3^-) for different concentrations. (CdI^+) is deduced from

$$(CdI^+) = (I^-) + (CdI_3^-) - 2(Cd^{++}).$$

Table III gives the values of (Cd^{++}), (I^-), (CdI_3^-) and (CdI^+) corresponding to total concentrations of CdI_2 ranging from 0.005 mol/l. to 0.5. The values obtained for this latter concentration must only be considered as approximations, one of the values for the E.M.F. having been determined by extrapolation.

TABLE III

Concentrations in Mols per Liter of each of the Ions present in Aqueous Solutions of Cadmium Iodide

Total cadmium	(I^-)	(Cd^{++})	(CdI_3^-)	(CdI^+)	Total CdI_2 dissociated
0.005	0.0063	0.00315	0.0000	0.0000	0.00315
0.01	0.0103	0.0037	0.0000	0.0029	0.0066
0.02	0.0148	0.0040	0.0011	0.0079	0.0130
0.05	0.0228	0.0048	0.0064	0.0196	0.0308
0.1	0.0252	0.0084	0.0153	0.0237	0.00474
0.2	0.0285	0.0138	0.0350	0.0359	0.0847
0.5	0.0181	0.0973	0.1769	0.0004	0.2746

In Table IV we give for comparison the conductivity ratios and the activity coefficients as calculated by Getman (loc. cit.) and the ratios $1/2C\left[(Cd^{++}) + (I^-)/2\right]$, where C is the total concentration of CdI_2, and also the ratios $1/C\left[(I^-) + (CdI_3^-)\right]$.

TABLE IV

Comparison of the Ionic Concentrations deduced from Migration Data and and E.M.F. with Arrhenius' Degrees of Dissociation and with Activity Coefficients

Total cadmium	Activity coefficients	$1/2C[(Cd^{++})+(I^-/2)]$	$1/2C[(I^-)+(CdI_2)]$	Conductivity ratios (25°C)
0.005	0.56	0.63	0.63	0.63
0.01	0.40	0.44	0.51	0.53
0.02	0.26	0.28	0.40	0.43
0.05	0.14	0.16	0.29	0.30
0.1	0.09	0.10	0.20	0.23
0.2	0.06	0.07	0.16	0.19
0.5	0.03	(0.11)	(0.19)	0.16

It is interesting to notice that the conductivity ratios and the values of $1/C\ [(I^-) + (CdI_3^-)]$ are in close agreement, and also that the activities calculated by Getman are of the same order of magnitude as the values of $1/2C\ [(Cd^{++}) + (I^-)/2]$. This seems to prove that, for CdI_2, the conductivity ratios fairly closely represent the percentage of ions present in the solution in Arrhenius' sense. The activity coefficients deduced from E.M.F. measurements correspond to the total percentage of the simple ions measured by the electrodes used, in this case Cd^{++} and I^-, and ignoring the complexes CdI^+ and CdI_3^-.

PART II

Table V contains diffusion coefficients measured for various concentrations of cadmium iodide, at 25°C., by the method of McBain and Liu.[1]

TABLE V

Concentration m/1.	Diffusion coefficients	Concentration, m/1.	Diffusion coefficients
0.005	0.956	0.05	0.788
0.005	0.964	0.05	0.790
0.005	0.965	0.15	0.732
0.005	0.951	0.5	0.690
0.01	0.859		

The diffusion coefficient corresponding to infinite dilution, i.e., to complete dissociation into Cd^{++} and I^- ions, is given by Haskell's equation for infinite dilution, which is an extension of the Nernst formula to the case of unsymmetrical salts:

$$D_\infty = RT\ \frac{m_{Cd^{++}} \cdot m_{I^-}}{m_{Cd^{++}} + m_{I^-}} \left(\frac{1}{2} + \frac{1}{1}\right)$$

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[1] J. W. McBain and T. H. Liu: J. Am. Chem. Soc., 53, 59 (1931).

At 25°C. the limiting mobility of I^- is 75.4. From the ratios of mobilities used in Part I we deduce

$$m_{Cd^{++}} = 61.6, \; m_{CdI_3^-} = 42.8, \; m_{CdI^+} = 22.0$$

At a finite concentration at which the only ions present are the simple Cd^{++} and I^- ions, the degree of dissociation being α, the part of the diffusion coefficient due to those ions is given by:

$$D = D_\infty \times \alpha$$

We have, at 25°C.:

$$D_\infty = 0.023 \times \frac{61.6 \times 75.4}{137.0}\left(\frac{1}{2}+\frac{1}{1}\right) = 1.170$$

McBain and Liu proposed the following general equation for the diffusion coefficient of any electrolyte at any concentration:—

$$D = \frac{iRT}{\Sigma \frac{C}{m}}$$

in which C is the fraction of the total concentration which is in the form of ions or molecules of mobility m. The summation is extended to all the ions, simple and complex, and to the neutral molecules. i is van't Hoff's coefficient. At any concentration of cadmium iodide where, beside neutral molecules, simple Cd^{++} and I^- ions only are present, this equation gives for 25°C.

$$D = \frac{0.023\,i}{\frac{2\alpha}{m_{I^-}} + \frac{2\alpha}{m_{Cd^{++}}} + \frac{1-\alpha}{m_{CdI_2}}}$$

i is deduced from freezing point measurements.[1] At the lowest concentration studied by us (0.005 molar)

$$i = 1 + 2 \times 0.63 = 2.26$$

In the first part of this paper we assumed as a first approximation, since the conductivity ratio is 0.63 at that concentration, that the degree of dissociation is equal to 0.63. Now we shall consider the degree of dissociation at 0.005 molar and the mobility of the CdI_2 molecule as two unknowns. We are going to determine their values by requiring that Haskell's formula and the McBain-Liu formula give at the concentration 0.005 molar the experimental value 0.959, recorded in Table V.

At 25°C. and 0.005 molar, $D_{Cd^{++}+I^-} = 1.17 \times \alpha$. The difference between 0.959 and $1.17 \times \alpha$ is then due to the diffusion of the neutral molecules. The mobility of the CdI_2 molecule must then be given by:

$$m_{CdI_2} = \frac{0.959 - 1.17\alpha}{(1-\alpha)\,RT} = \frac{0.959 - 1.17\alpha}{0.023\,(1-\alpha)}$$

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[1] Compare J. W. McBain: Z. Elektrochemie, **11**, 215 (1905).

We then have the two simultaneous equations:

$$\begin{cases} 0.959 = \dfrac{2.26 \times 0.023}{\dfrac{2\alpha}{75.4} + \dfrac{2\alpha}{61.6} + \dfrac{1-\alpha}{m_{CdI_2}}} \\[2ex] m_{CdI_2} = \dfrac{0.959 - 1.17\alpha}{0.023\ (1-\alpha)} \end{cases}$$

or

$$\begin{cases} \alpha m_{CdI_2} - 0.921\ m_{CdI_2} - 17\alpha + 17 = 0 \\ \alpha m_{CdI_2} - m_{CdI_2} - 50.9\alpha + 41.6 = 0 \end{cases}$$

These two equations represent hyperbolae. Drawing the two curves, one finds for their intersection point:

$$m_{CdI_2} = 22.3$$
$$\alpha = 0.675$$

The actual degree of dissociation at the concentration 0.005 molar is thus, as expected, a little higher than the conductivity ratio 0.63. All our calculations in Part I could be modified accordingly. We will not do so, because the new value obtained for the degree of dissociation at the concentration 0.005 molar is probably not yet the final one. We only attempt to calculate as well as possible the orders of magnitude of the concentrations of the various ionic species. Taking the concentrations given in Table IV (except for the 0.005 molar solution for which the new value of the degree of dissociation is used) the diffusion coefficients listed in Table IV are obtained from the McBain-Liu formula.

Table VI

Concentration, mols per liter	van't Hoff's i	D calculated	D measured or interpolated
0.005	2.26	0.959	0.959
0.01	2.08	0.883	0.859
0.02	1.88	0.844	0.831
0.05	1.52	0.740	0.789
0.1	1.25	0.654	0.750
0.2	0.96*	(0.524)	0.720

* By extrapolation.

The results show that at low concentrations the agreement is to be regarded as fairly satisfactory. It should be pointed out that the calculated values are exceedingly sensitive to a slight change in the mobility of one of the constituents. If, for instance, we deduce the mobility of the CdI_2 molecule from Haskell's formula and from the value 0.63 for the degree of dissociation of 0.005 molar CdI_2, we find 26.1 This value when used in the McBain-Liu formula for the concentration 0.005 molar gives 1.02 for the diffusion coefficient instead of 0.959.

It is probable that if all the concentrations given in Table IV were corrected by taking 0.675 instead of 0.63 for the degree of dissociation of 0.005 molar CdI_2, a better agreement between calculated and measured values of the diffusion coefficient than that shown in Table VI would be obtained; this because of the fact that the term corresponding to the molecules CdI_2 in the McBain-Liu formula would be decreased.

However, the chief reason for the very significant difference between observed and calculated values for higher concentrations is that the observed values were obtained by diffusion into pure water instead of into slightly less concentrated cadmium iodide. The experimental data are therefore integral values, whereas those calculated refer only to the concentration indicated. McBain and Liu have shown for other cases that integral values diverge in this manner.

On the whole the preceding calculations show that the concentrations of the various ionic species calculated in Part I give reasonably good values of the diffusion coefficients.

Summary

(1) Measurements have been made of the E.M.F. of cells containing cadmium iodide in concentrations from 0.001 to 0.4 molar. These measurements have been combined with those for other cells measured by Getman to deduce the concentrations of the simple ions.

(2) Using the general formulation of migration of Laing and McBain, the concentrations and mobilities of the complex cations and anions have been evaluated.

(3) It is found that the sum of the concentrations of the simple ions follows closely or is equal to the activity coefficients and that, further, for the weak electrolyte, cadmium iodide, the total dissociation is substantially in agreement with (and slightly more than) the conductivity ratio of Arrhenius.

(4) Diffusion coefficients have been measured for solutions of cadmium iodide for concentrations from 0.005 to 0.5 molar. From these measurements and from the combination of the Haskell and McBain-Liu diffusion formulae the mobility of the cadmium iodide molecule and a more accurate value of the degree of dissociation of 0.005 molar cadmium iodide have been deduced. The concentrations of the various molecular species present in solutions of cadmium iodide have been used to calculate the diffusion coefficients. Fairly good agreement with the experimental values has been obtained.

(5) The behavior of cadmium iodide with respect to the dissociation and formation of complexes differs only in degree from that of all other salts containing divalent ions.

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COPPER QUADRANTOXIDE

BY M. J. MURRAY

Mellor[1] is not very certain that there is such a substance as copper quadrantoxide, Cu_4O. "H. Rose[2] prepared what he regarded as copper quadrantoxide, Cu_4O, or copper tetritaoxide, by adding freshly prepared and moist cuprous chloride to a dilute solution of stannous chloride in potassium hydroxide; if the solution be not dilute enough or if too much stannous chloride be employed, metallic copper is precipitated. The same product was obtained by using a solution of cuprous sulphate instead of cuprous chloride. . . . Gladstone and Tribe[3] also say that if a copper-silver couple be placed in a solution of cupric nitrate, a film of this oxide may be deposited on the silver plate. Recoura[4] obtained Rose's oxide by the decomposition of cuprous oxide. Rose thus describes the properties of copper quadrantoxide. The olive-green powder is stable if kept under water out of contact with air, and it gradually becomes denser and less readily oxidized; but it cannot be dried without change. When the oxide is heated in a limited supply of air, it acquires a yellow film of cuprous oxide. Dilute sulphuric acid converts it into copper and cupric sulphate in the proportions $Cu:CuSO_4 = 3:1$ (nearly); the equation is presumably $Cu_4O + H_2SO_4 = 3Cu + CuSO_4 + H_2O$. Since cuprous oxide is soluble in dilute sulphuric acid, Moser[5] says that the quadrantoxide is either decomposed by the dilute acid or else it is a mixture of cuprous oxide and copper. Hydrochloric acid first darkens the quadrantoxide—possibly forming copper subchloride—and then furnishes a mixture of copper and cuprous chloride; and hydrocyanic acid forms a black substance—possibly copper subcyanide—soluble in dilute nitric acid. Hydrogen sulphide transforms copper quadrantoxide into a black homogeneous substance—possibly copper subsulphide—which gradually gives off hydrogen and forms a higher sulphide. The quadrantoxide is insoluble in aqua ammonia or in an ammoniacal solution of ammonium carbonate. Gladstone and Tribe add that silver nitrate is reduced to filiform silver by copper suboxide. Analyses of the product correspond with 95 percent Cu_4O and 5 percent stannous oxide. The chemical individuality of the quadrantoxide has not therefore been established, and, when further investigated, it may prove to be a hydrogel of variable composition. Wöhler and Balz[6] observed no signs of the quadrantoxide in their study of the dissociation $2CuO \rightarrow Cu_2O \rightarrow 2Cu$."

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[1] "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", **3**, 116 (1923).

[2] Pogg. Ann., **120**, 1 (1863).

[3] Chem. News, **25**, 193 (1872).

[4] Compt. rend., **148**, 1105 (1909).

[5] Z. anorg. Chem., **64**, 200 (1909).

[6] Z. Elektrochemie, **27**, 406 (1921).

Moser[1] is quite definite as to the non-existence of copper quadrantoxide. "When cupric or cuprous compounds are reduced by stannous salts in alkaline solution or by sodium hydrosulphite in presence of hydroxyl ions, one gets no quadrantoxide, but mixtures of cuprous oxide and copper, or only metallic copper. It is easy to understand the error made by Rose in thinking that he had a lower oxide of copper, because many of the properties of the mixtures could be considered as those of a lower oxide. Especially significant is the fact that the green precipitate turns yellow when the surface is exposed to the air. If hydroxyl ions are present, this process takes place more rapidly, and the finely divided copper is oxidized to the yellow cuprous oxide. This can easily be observed if one adds ammonia to the green, washed, precipitate. In the absence of air there is no change in a short time. If oxygen gets in, there is, almost suddenly, a formation of amorphous, yellow, cuprous oxide at the surface of the suspension. It was this process that Rose considered as the oxidation of the lower oxide when he added ammonia to the wash-water in order, as he says, to make the precipitate agglomerate more readily. Since the concentration of ions in the liquid was very low because of the repeated washings, addition of ammonia, an electrolyte, causes the hydrosols of copper and cuprous oxide to form gels. The precipitate becomes, as Rose says, 'denser' as it settles to the bottom. On the other hand, if ammonia is added with the most scrupulous exclusion of air, only a small portion of the cuprous oxide dissolves to form the complex molecules $(Cu.nNH_3).OH$. This increases the relative amount of copper in the precipitate, which thereby becomes more dense and consequently settles more rapidly. The further observation by Rose that addition of hydrochloric acid dissolves the quadrantoxide to a dark-colored subchloride, which soon decomposes with precipitation of copper and formation of cuprous chloride is true to the extent that the copper comes out at first in a colloidal form on addition of hydrochloric acid to the amorphous cuprous oxide gel, so that it looks as though one had a dark-colored solution.

"The two, practically identical, results which Rose obtained by decomposing the substance with dilute sulphuric acid in the absence of air, can be accounted for because Rose worked to a definite, green color of the precipitate, which therefore corresponded in the two cases to the same amounts of the two components.

"By mixing finely divided copper with yellow cuprous oxide it was possible to obtain mixtures which had identically the same properties as the hypothetical quadrantoxide. If the solution is alkaline, the finely divided copper on the surface oxidizes on the surface to cuprous oxide and one believes that the green precipitate becomes yellow in contact with the air. Also, on addition of ammonia, the same phenomena occur as have been described. On addition of sodium thiosulphate, it is possible to dissolve the cuprous oxide with formation of complex ions, leaving the finely divided copper behind. This phenomenon, which was observed in both cases, is characteristic of a mixture."

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[1] Z. anorg. Chem., **64**, 212 (1909).

The preceding paragraph is a very disappointing one. Moser does not say how he made his finely divided copper or in what proportion he mixed it with his also undescribed cuprous oxide. If the copper was not of the same grain size as in Rose's alleged compound, the two colors cannot have been identical. If it was of the same particle size, Moser has not offered any proof that his mixture remained a mixture. It may have reacted to form the quadrantoxide. It is probable that Moser had a mixture; but there is a difference between probability and proof, and Moser has overlooked that difference. While sodium thiosulphate would dissolve cuprous oxide out of a mixture of cuprous oxide and copper, it might also dissolve it out of a compound. We have a double salt, $CuCl_2.2KCl.2H_2O$, even though absolute alcohol will dissolve the cupric chloride and leave the potassium chloride behind. Moser would have concluded from this experiment that he had a mixture of cupric chloride and potassium chloride, and he would have been wrong even if he had mixed his two salts in presence of a trace of water. Moser's conclusion that there is no definite copper quadrantoxide is not justified by his experiments.

Some years ago, Mr. J. Y. Riffe, now of Charleston, West Virginia, did some work on this problem while a graduate student at the University of Colorado, under the direction of Professor F. E. E. Germann. The results were never published and Mr. Riffe very courteously placed them at the disposal of Professor Bancroft. It was to supplement this material that I did the few experiments which will be described later.

Mr. Riffe points out that "Sabatier and Espil[1] proved, to their own satisfaction, that the suboxide of nickel, Ni_4O, is a definite compound by means of the data obtained by the reduction of nickel oxide by hydrogen, plotting percentage reduction against time, and observing that a more or less definite break occurred in the curve at about 70-75 percent reduction. This evidence was sufficient for Rideal and Taylor[2] to take up the study of nickel as a catalyst from the standpoint of the formation of Ni_4O as an intermediate compound."

Chiefly on the basis of the work by Wöhler and Balz,[3] the existence of nickel quadrantoxide as a definite chemical compound is discredited by Roscoe and Schorlemmer[4] and by Wagner.[5]

Mr. Riffe goes on to say that "as copper is next to nickel in importance as a catalyst in organic synthesis, Sabatier and Espil attempted to prove the existence of Cu_4O in the same way, by the reduction curve. In this they were not very successful as the curve failed to show signs of a break, although a critical examination of the points of reference of their published curve seems to indicate that they might just as well have drawn straight lines with breaks at fifty and seventy-five percent reductions corresponding to the compounds, Cu_2O and Cu_4O.

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[1] Compt. rend., **159**, 668 (1914).

[2] "Catalysis in Theory and Practice,"

[3] Z. Elektrochemie, **27**, 406 (1921).

[4] "Treatise on Chemistry," **2**, 1370 (1923).

[5] Thorpe: "Dictionary of Applied Chemistry," **4**, 530 (1922).

"The most extensive and thorough work on the reduction of copper oxide by hydrogen was done by Wright, Luff and Rennie.[1] Their investigation covered a wide range of conditions, temperatures, rate of gas flow, etc. They came to the conclusion that the reduction curve was without breaks. However, in no case did they make the reduction slower than about six hours for about ninety percent reduction. Pease and Taylor[2] repeated part of the work of Wright, Luff and Rennie, with the object of studying the action at the Cu-CuO interface, and the inhibiting action of water vapor and oxygen upon the rate of reduction. They verified the previously made observation that, after a period of incubation during which there was apparently no reduction, the reaction started from minute particles of a red color within the mass of oxide and spread in all directions. This was thought to be conclusive evidence that the reaction went much more rapidly at a copper-copper oxide interface and they verified this conclusion by mixing with the copper oxide some completely reduced copper, a proceeding which shortened the period of incubation.

"From the data given in the experimental part of this article and from the fact that cuprous oxide can also be red, it may well be that the reduction spread from the CuO-Cu_2O interface. In fact, our results seem to permit no other interpretation. However, no method other than interpretation of the curve suggested itself for proving this point. If some Cu_2O were to be mixed with the CuO, one would not expect a long period of incubation before reduction began.

"With all the above in mind, we wished to prove the existence of the lower oxide of copper, Cu_4O, both by reduction and by oxidation methods. One of us [Riffe] had observed several years ago that a freshly prepared solution of copper in ammoniacal copper sulphate would precipitate metallic copper if acidified, and that the amount of precipitate depended upon the time which had elapsed between dissolving the copper and acidification. This promised to be a convenient method for studying the rate of oxidation of copper in solution. The only method which readily suggested itself for studying the rate of reduction was by the often-tried one of reduction of the oxide in a stream of hydrogen; but this had been done so often and so well that it seemed rather presumptuous to expect any new light from it. However, we could not help but feel that the rate of reduction should show up differently for the different oxides of copper and that, if we could get the proper conditions for bringing out the presence of the well-known oxide, Cu_2O, we might be able to do likewise for the less stable oxide, Cu_4O. So at first our attention was directed to reduction under some possible conditions for bringing out the presence of cuprous oxide. The catalytic action of interfaces and of water vapor was minimized as far as possible by suitably designed apparatus, and, when the reaction velocity was slowed down to about one-fourth of that used by previous workers, we were able to get results that indicated not only the presence of Cu_2O very clearly, but also that of the lower oxide, Cu_4O.

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[1] J. Chem. Soc., **35**, 475 (1879).

[2] J. Am. Chem. Soc., **43**, 2179 (1921).

"In both the oxidation and the reduction investigations, it was found that one-fourth of the oxygen carried by cupric oxide was bound to the copper more firmly than the rest. To be more exact, it was found that this much of the oxygen was dislodged at a slower rate than the rest, and taken up at a much faster rate, other conditions being fairly constant. We are of the opinion that this is rather definite proof of the existence of the suboxide of copper, copper quadrantoxide, under certain definite, but rather limited, conditions."

Mr. Riffe describes the following experiments on oxidation. "A solution of ammoniacal cupric sulphate, of known copper value, was heated to some definite temperature between 40° and 80°, and a stirring device, fashioned out of copper gauze and copper wire, was rotated rapidly in it for a definite length of time. A certain amount of copper was dissolved from the stirrer, the amount depending on the temperature of the solution and the concentration of the copper sulphate. The amount of copper dissolved was determined by weighing the stirrer before and after. The ammoniacal solution containing the dissolved copper was allowed to stand for definite lengths of time, which varied from only a few seconds to several hours, during which it absorbed oxygen rapidly from the air. Sulphuric acid (1:1) was then added until the solution became neutral or slightly acid. At the neutral point a heavy precipitate of metallic copper was thrown down.

"When the copper sulphate solution was filtered off and tested for copper, it was found that there was an appreciable increase in strength, and the sum of the copper precipitated and that found in the increase of copper sulphate in solution was, of course, equal to the total copper dissolved. The ratio of the amount precipitated and that dissolved was found to be a variable one. This variable was a function of the time allowed for the dissolved copper to oxidize by absorption of atmospheric oxygen. The percentage of the total dissolved copper which could be precipitated varied from seventy-five percent, if precipitated immediately after solution, to zero if allowed to stand for several hours."

Mr. Riffe's explanation of the phenomenon is not right. He postulates that no copper would dissolve from the stirrer in the absence of oxygen, which is not true. He also postulates that the copper dissolves as Cu_4O, which may be true but which is not necessarily so.

What actually happens when air is excluded is that metallic copper reduces the ammoniacal cupric oxide to cuprous oxide which of course in moderate concentrations remains in solution. One equivalent of copper dissolves and the solution becomes colorless. On acidification the following reaction takes place:

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$$

The one equivalent of copper which dissolved is reprecipitated and the original concentration of copper compound is again produced.

Of course if air is allowed to come in contact during the stirring, the solution will not become colorless, i.e., oxidation will proceed continuously, with the result that not all of the copper which dissolves can be reprecipitated as metallic copper. The solution when acidified will show more and more cupric compound. If the correct amount of air is stirred in only 75% of the copper which dissolved will be reprecipitated and it might appear that the copper had dissolved as quadrantoxide; but if no air is stirred in or allowed to enter after the reduction, all the copper is reprecipitated.

Experiments designed to illustrate this were conducted as follows: 25 cc. of an approximately M/10 $CuSO_4$ solution were put in a 50 cc. wide-mouth, glass-stoppered bottle. A roll of freshly-cleaned, weighed copper gauze was put in the copper sulphate solution and the bottle filled with concentrated ammonium hydroxide. This operation was carried on in an atmosphere of hydrogen and the solutions were freed of air before using. The bubble entrapped when the stopper was inserted being hydrogen could not cause oxidation. The bottle and contents were shaken at room temperature, 20°C, and in a few minutes the solution had become entirely colorless. Shaking was continued for two hours. At the end of this time the bottle was opened, again in an atmosphere of hydrogen and the contents poured into a beaker containing dilute sulphuric acid in slight excess of the amount required to neutralize the ammonium hydroxide.

The loss in weight of the copper gauze was 160 milligrams while 25 cc. of the $CuSO_4$ solution used contained by electrolytic determination of the copper, 156 milligrams. Considering the great affinity which the solution has for oxygen the slight difference is readily accounted for.

Another experiment in which air was purposely allowed to enter showed that the amount of copper dissolved was increased just as it should be.

One other experiment was tried in this line—that of using dilute ammonium sulphate solution instead of the copper sulphate solution. In this case only a very slight trace of copper dissolved from the roll of gauze.

Mr. Riffe also made a study of the rate of reduction of cupric oxide in an atmosphere of hydrogen. "The apparatus was designed to eliminate as far as possible the effect of the heat of reaction and of the water vapor formed. This was done by spreading the material over the bottom of a 500 cc. flask. We also wanted to study the effect of the rate of flow of the gas stream, the difference in rate of reduction at different temperatures, and, particularly, to have an apparatus that would operate over hours and even days under absolutely uniform conditions. The set-up which answered our purpose very well was constructed as shown in Fig. 1. The hydrogen from the tank flowed throughout a "Purox" pressure reducer, set so that the gauge B gave two pounds pressure to the line through a glass stop-cock which could be adjusted for any rate of flow, then through a differential flow-meter of the type shown. This flow-meter gave reasonably accurate readings for rates of flow from ten to a hundred cc of hydrogen per minute and was made by inserting a piece of capillary tubing of about .25 mm bore between two lengths of ordinary size tubing and by-passing with a small-size tubing which ran into an oil reservoir at an angle of about 10°. The reservoir was filled with a light non-volatile oil (3 in 1), up to the zero mark on the sloping tube. It was calibrated by finding the depression of the oil column for four known rates of flow into a gasometer and then constructing the straight line curve. After passing the flow-meter, the hydrogen was passed into a combustion tube and across a platinum wire heated electrically to a white heat. This served to transform the small amount of oxygen present into water, which was then removed by passing the gas through a U-tube filled with phosphorus pentoxide. The dried and purified gas was then run into the reaction flask placed in a Freas constant-temperature oven. The copper oxide was scattered over the bottom of the flask in a thin layer. The hydrogen, plus the water vapor formed in the reduction, was then passed through one or two tared U-tubes connected into the chain in parallel and containing P_2O_5, through another flow-meter to get an estimate of the amount of hydrogen used up and to have a quick method of detecting leaks in the apparatus, and then to the atmosphere. After given intervals of time the tared U-tubes H and J were wiped to constant weight and accurately weighed. Care was taken at this point to weigh the tubes after intervals of not more than ten minutes from the time they were removed from the apparatus and placed in the balance case in order to minimize as far as possible the diffusion of hydrogen. The difference in weight of the U-tube filled with hydrogen and filled with air was greater than the usual amount of water vapor caught.

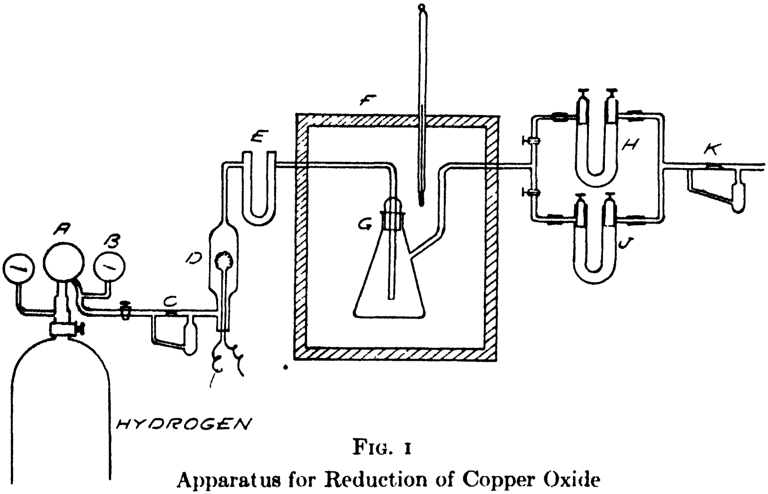

Fig. 1

Apparatus for Reduction of Copper Oxide

A—Tank pressure reducer
B—Line pressure gauge
C—Differential flowmeter
D—Oxygen remover
E—Phosphorus pentoxide
F—Freas electric oven
G—Reduction flask
H—Phosphorus pentoxide tube
J—Same
K—Differential flowmeter

"The advantages of having the copper oxide scattered over the bottom of a large flask are very apparent: the heat of reaction does not affect the temperature of the rest of the copper oxide to an appreciable extent, the water vapor formed rises immediately out of the reaction zone, and, as the oven was equipped with a glass door, the progress of the reaction could be observed.

"Fig. 2 was plotted from results obtained by exceedingly slow oxidation. As a further precaution towards minimizing the influence of interface catalysis the sample of CuO was ground in a pebble mill with SiO_2 for a couple of hours. The reducing value of this mixture was determined by reduction of a weighed sample at a temperature of 250° in hydrogen, and as a check, by an electrolytic determination of the copper. The copper oxide used was a sample of Kahlbaum finely-ground reagent which analyzed 19.4 per cent available oxygen. About four parts SiO_2 to one part CuO was used. The reduction was carried on at 130°C. The hydrogen flow was 45 cc/min.

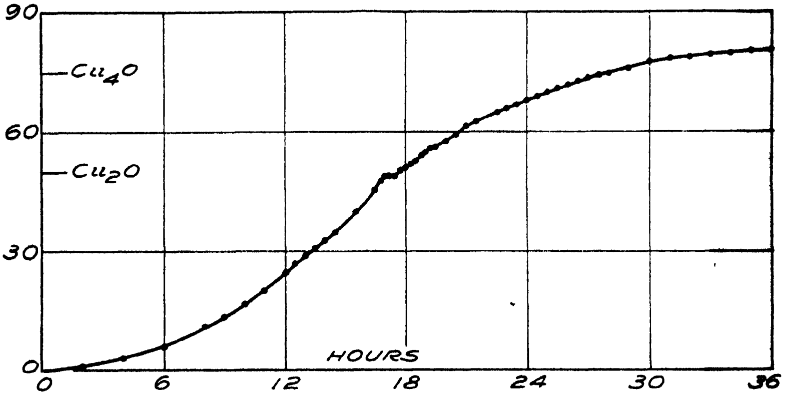

FIG. 2
Copper Oxide Reduction

"This curve can be divided into three parts: the first part starts from CuO which is reduced very slowly at the start but with perfectly regular increasing acceleration until a maximum rate is reached just before the point of half reduction. This corresponds to the conversion of all the CuO to Cu_2O if the mass is homogeneous throughout, and as the time necessary for reaching this stage is a matter of some 16 hours it is safe to assume homogeneity. When all the copper is in the form of Cu_2O there is a very decided decrease in the rate of reduction, amounting in this case to actual cessation for a period of half an hour. Then there is a short period of fluctuating rates of reduction (clearly shown in Fig. 3 which is a section of the same curve on a large scale) followed by an increasing rate of reduction until a maximum is reached which is about half the value reached in the previous maximum, then there is a gradual but uniformly decreasing rate of reduction until in the vicinity of 75 per cent reduction the rate reaches a value of about 5 per cent of the maxima. This point corresponds to the formation of Cu_4O. From this point the rate of reduction becomes constant within the limits of experimental error and the curve continues in a straight line. This last statement about the straight line may be subject to correction if we ever have the time, patience, and luck to keep the apparatus going long enough to determine a

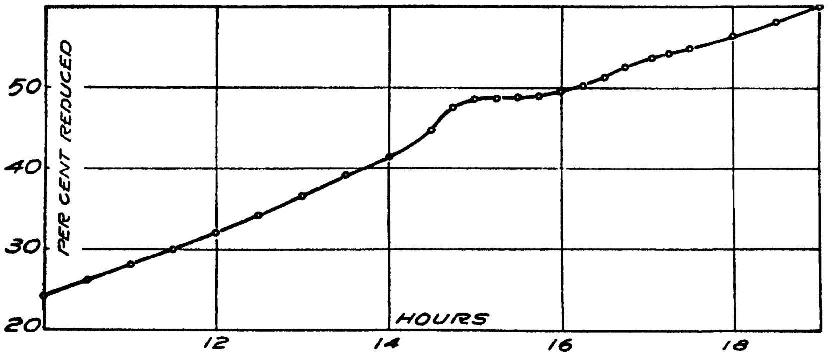

Fig. 3
Copper Oxide Reduction
Temperature 130°.
Hydrogen Flow 45 cc/min.
Diluted with SiO_2.

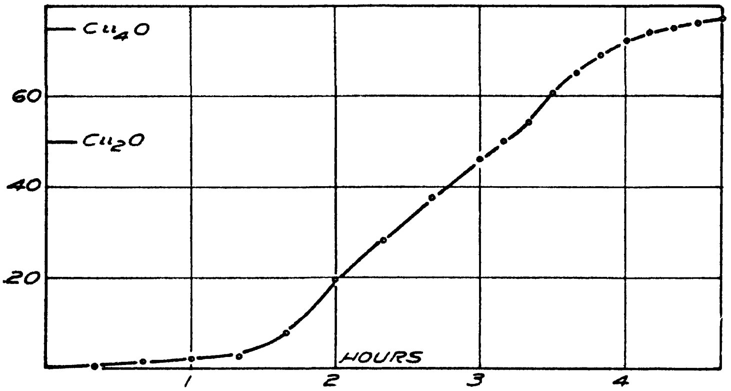

Fig. 4
Copper Oxide Reduction

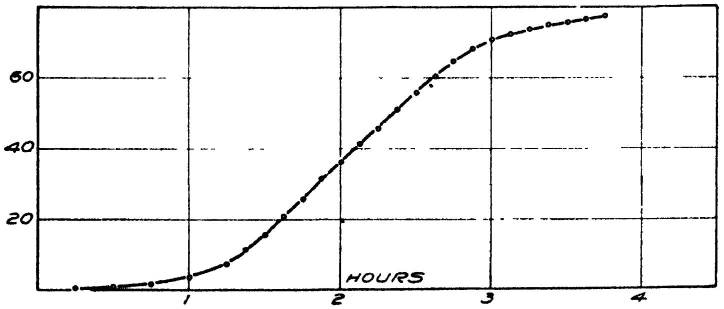

Fig. 5
Copper Oxide Reduction

TABLE I

Hours	Water gms × 10^{-4}	Total Water gms × 10^{-4}	Reduction per hour	Percent Reduction
2:00	11	11	0.25	0.5
4:00	46	57	1.2	2.7
6:00	57	114	1.5	5.3
8:00	102	216	2.7	10.6
9:00	63	279	3.1	13.1
10:00	75	354	3.5	16.5
11:00	73	427	3.4	19.9
12:00	73	530	3.4	24.7
12:30	40	570	3.7	26.6
13:00	40	610	3.7	28.5
13:30	42	652	3.9	30.5
14:00	44	696	4.1	32.5
14:30	46	742	4.3	34.7
15:30	106	848	5.0	39.7
16:30	122	970	5.7	45.3
16:45	56	1026	10.5	47.9
17:00	20	1046	3.7	48.8
17:15	0	1046	0.0	48.8
17:30	0	1046	0.0	48.8
17:45	14	1070	2.6	50.0
18:00	10	1080	1.9	50.5
18:15	20	1100	3.7	51.4
18:30	18	1118	3.4	52.2
18:45	28	1146	5.3	53.6
19:00	24	1170	4.5	54.7
19:15	10	1180	1.9	55.1
19:30	14	1196	2.6	55.8
20:00	32	1228	3.0	57.4
20:30	38	1266	3.6	59.1
21:00	40	1304	3.7	61.0
21:30	28	1332	2.6	62.3
22:30	48	1380	2.2	64.5
23:00	22	1402	2.1	65.5
23:30	26	1428	2.4	66.7
24:00	20	1448	1.8	67.6
24:30	24	1472	2.2	68.8
25:00	20	1492	1.9	69.8
25:30	20	1512	1.9	70.7
26:00	16	1528	1.5	71.3
26:30	20	1548	1.9	72.3
27:00	16	1564	1.5	73.1
27:30	18	1582	1.7	74.0
28:00	16	1598	1.5	74.7
29:00	32	1630	1.5	76.0
30:00	32	1662	1.5	77.6
31:00	13	1675	0.61	78.3
32:00	11	1686	0.51	78.8
33:00	12	1698	0.56	79.3
34:00	10	1708	0.48	79.8
35:00	9	1717	0.43	80.3
36:00	10	1727	0.48	80.7

sufficient number of points in such a slowly moving reaction. However, several runs each lasting several days with points at six and twelve hour intervals give an exactly straight line. If this reaction is to be explained by interface catalysis at all, under these conditions, it is necessary to make the compound Cu_2O the accelerating medium. As the amount of this substance increases, the rate of reduction increases until a maximum rate is reached just before all the cupric oxide is converted into the cuprous form. Then there is a state of equilibrium with no reaction taking place until a small nucleus of the still lower oxide is formed. A maximum reduction is soon reached under these conditions which when there is almost exactly half Cu_2O and half Cu_4O, then the rate of reduction gradually decreases as the amount of Cu_2O becomes smaller until a constant value is obtained when there is nothing but Cu_4O present. From the fact that the rest of the curve is a straight line, we assume that there is no accelerating effect due to the presence of metallic Cu in with the Cu_4O as the reduction proceeds.

TABLE II

Two-gram sample of the oxide dried at 135°C. Temperature of reduction 127°

Time in Hours	Water in gms. $\times 10^{-1}$	Total Water gms $\times 10^{-4}$	Reduction per hour	Percent Reduction
:20	22	22	1.5	.5
:40	30	52	2.1	1.2
1:00	36	88	2.5	2.0
1:20	36	124	2.5	2.8
1:40	224	348	15.4	8.0
2:00	516	864	35.5	19.5
2:20	366	1230	25.2	28.1
2:40	424	1654	29.2	37.9
3:00	358	2012	24.6	46.1
3:10	192	2204	26.4	50.5
3:20	176	2380	24.2	54.5
3:30	272	2652	37.4	60.8
3:40	200	2852	27.5	65.3
3:50	178	3030	24.4	69.3
4.00	116	3146	15.9	72.2
4:10	94	3240	12.9	74.2
4:20	48	3288	6.6	75.2
4:30	46	3334	6.3	76.3
4:40	44	3378	6.0	77.2
6:10	118	3496	1.8	79.3

"Fig. 4 is plotted from the results obtained with the same sample of copper oxide, reduced at the same temperature and with the same rate of gas flow: the only difference being that it was not diluted with SiO_2. This curve has the same characteristics as Fig. 2, but it will be noticed that the time of reduction is very materially reduced and the break at the point corresponding to half reduction is less noticeable.

"Attempts were made to slow down the rate of reduction by reducing the temperature in order to get a curve which would have the same time factor as curve 1 but without success. This was principally due to the fact that the change in rate of reduction per degree difference in temperature increased very rapidly in the region of 120°-130° and the constant-temperature oven available would not permit of sufficiently accurate adjustment.

"Fig. 5 is plotted from the results of work duplicating as nearly as possible the conditions under which previous investigators worked and confirms their conclusions that there is no break in the reduction curve as carried out by them.

"The accompanying Tables I, II and III contain the data from which curves 1, 3 and 4 are plotted.

TABLE III

One-gram sample of the oxide dried at 135°. Temperature of reduction 132°

:15	6	6	1.1	.2
:30	10	16	1.8	.7
:45	16	32	2.9	1.4
1:00	42	74	7.7	3.4
1:15	88	162	16.1	7.4
1:22	88	250	32.2	11.5
1:30	94	344	34.4	15.8
1:37	112	456	41.0	20.9
1:45	104	560	38.1	25.6
1:52	116	676	42.5	31.1
2:00	112	788	41.0	36.1
2:07	108	894	39.5	41.0
2:15	104	998	38.1	45.6
2:22	120	1118	43.9	51.0
2:30	100	1218	36.6	55.7
2:37	102	1320	37.3	60.4
2:45	92	1412	33.7	64.7
2:52	70	1482	25.6	68.0
3:00	56	1538	20.5	70.4
3:07	40	1578	14.6	72.2
3:15	32	1610	11.7	73.7
3:22	28	1638	10.2	75.0
3:30	22	1660	8.1	75.8
3:37	12	1672	6.7	76.5
3:45	12	1684	6.7	77.1

"Since the above was written, our attention has been called to an article by W. G. Palmer[1] in which he studied the oxidation of copper and the reduction of copper oxide by precipitating a very thin film of the metal on a china rod and observing the course of the oxidation or reduction by means of measuring the changes in reductance of the film. He confirms our observation that in the oxidation process the rate of oxidation is very high at first but he does not draw the same conclusion from this fact. He states that the rate of oxidation is abnormally high due to two causes: first, the increase of resistance of the film owing to the increase of temperature, and secondly, the stimulating effect of the reducing agent remaining in the film and rod on the oxidation.

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[1] Proc. Roy. Soc., 103A, 444 (1923).

"The curves for the reduction which he reproduces are, in the main, similar to those already published and show no break for the oxides. This is not surprising when we consider that he was able to get only a very few hasty readings in the ten minutes or so necessary to reduce the film completely.

"In general it might be said that Mr. Palmer's view as to the mechanism of the reduction of copper oxide by hydrogen does not coincide with those of Pease and Taylor nor with the evidence presented in this article. The method which he used, however, seems to promise excellent results if the reaction on such a thin film could be slowed down sufficiently to permit of a sufficient number of accurate readings."

While these curves may make it probable that copper quadrantoxide exists, the breaks in the curves as plotted are not marked enough to be very convincing. It seemed desirable to find some other method which would be less arbitrary. Such a method had been suggested implicitly by Rose when he said that the precipitate which he called copper quadrantoxide did not dissolve in ammoniacal solutions, which do dissolve cuprous oxide. Since there are a number of cases in which a precipitate, once formed, does not dissolve readily, it seemed best to work under conditions which preclude the formation of the wrong precipitate. If we take an ammoniacal solution of cuprous oxide and reduce it still further we cannot, by definition, get a mixture of copper and cuprous oxide precipitating. We shall get a one-phase precipitate either of copper quadrantoxide or of metallic copper.

N/10 $CuSO_4$ solution was made strongly ammoniacal and dilute sodium hydroxide was added. Then sodium hydrosulphite was added as the reducing agent. The deep blue color first disappeared and on further addition of reducing agent metallic copper (not an olive green precipitate) was obtained. If Cu_4O had formed and could possibly have remained in the solution, metallic copper could not have made its appearance on the addition of a little more than one equivalent of the reducing agent. Besides the compound is supposed to be insoluble in NH_4OH.

If in the above experiment the ammonium hydroxide is omitted, an olive green precipitate is obtained.

In an additional experiment the first step in the reduction of the copper was carried out in ammoniacal solution by means of a roll of copper gauze. To the colorless solution was added dilute sodium hydroxide and a small amount of sodium hydrosulphite. Metallic copper alone was precipitated.

While we do not know why the precipitate of the so-called copper quadrantoxide is olive-green, there is a very similar case cited by Roscoe and Schorlemmer.[1] "When powdered sulphur and fine copper-filings are well mixed together, a green-colored powder results, in which, however, a microscope will show the particles of sulphur lying by the side of the particles of copper." Professor Clyde Mason suggests that the copper particles act like a black, thus giving an olive green.

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[1] "A Treatise on Chemistry," 1, 47 (1920).

The significance of the results is unmistakable. When the solution is able to dissolve or peptize cuprous oxide, metallic copper appears as solid phase. When the solution cannot dissolve or peptize cuprous oxide, an olive-green precipitate is obtained. Since this must contain metallic copper, the other constituent cannot be copper quadrantoxide but must be a mixture.

The general results of this paper are:

1. The evidence proves that copper quadrantoxide does not occur as a stable solid phase at room temperature.
2. Rose's experiments to show that copper quadrantoxide can be made to precipitate from an alkaline solution and cannot be dissolved or peptized by ammoniacal solutions are vitiated by adsorption and therefore prove nothing.
3. Metallic copper precipitates when a cuprous salt is reduced in an alkaline solution under conditions such that cuprous oxide cannot precipitate. An olive-green precipitate is obtained when cuprous oxide can precipitate.
4. The olive-green precipitate cannot be copper quadrantoxide and must be a mixture of metallic copper and hydrous or anhydrous cuprous oxide.

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SOLUTIONS FOR COLORIMETRIC STANDARDS. IV.

Some Factors affecting the Color of Indicator Solutions*

BY M. G. MELLON AND G. W. FERNER

In some earlier work it was observed that certain indicators intended for use in the colorimetric determination of hydrogen ion concentration seemed to give erroneous results for the pH range through which they were supposed to undergo their transformation of color. The variation in hue for the same indicator supplied by different manufacturers was particularly disturbing.

This experience raised the question as to whose indicators one might use with most assurance, and whose method of use should be followed. If either or both of these points are of significance, any information regarding them should be of interest to individuals in various kinds of experimental work involving the use of such compounds. It is of special importance to those attempting to prepare permanent standards designed to match the color of indicator solutions.

The present work was undertaken with the object of securing information regarding the effect on certain indicator solutions of the following factors: (1) the source (or degree of purity) of the indicator itself; (2) the method of preparation of the stock solution of any given indicator; and (3) aging, particularly the effect of light.

Previous Work

Of the earlier relevant work mention may be made of some of the significant contributions. Several authors have noted variations in the hue of indicators from different sources. Hunter,[1] on testing samples of congo red from four manufacturers, found a divergence of 40 to 75 percent from the hue values for a purified product. Methyl orange showed a similar variation. After testing six different samples Collins[2] stated that methyl orange for indicator work should be so specified when ordering. Schlegel and Steuber[3] found that brom thymol blue from different sources, or successive lots from the same source, may give widely divergent results.

Similar observations have been made upon the method of preparing the stock solutions of indicators, and the effect of different substances, such as ethanol, upon the change of hue of indicators. Thiel and Springemann,[4] Thiel, Wülfken and Dassler,[5] and Michaelis and Mizutani[6] investigated the effect of ethanol. Kolthoff[7] states that little is known about the influence of different solvents on the sensitivity of indicators. Although he has called attention to a significant "alcohol error" for several indicators in solutions containing from 10 to 70 percent alcohol, the concentration is very much less than the smaller of these values when one is using one ml. of a 95 percent alcoholic solution in 50 ml. of a buffer solution. Clark[8] states that brom cresol purple dissolved directly in alcohol has a different hue than when prepared according to his method.

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* Presented before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society at Cincinnati, Ohio, September 8-12, 1930.

[1] Biochem. J., **19**, 42 (1925).

[2] J. Ind. Eng. Chem., **12**, 800 (1920).

[3] Ind. Eng. Chem., **19**, 631 (1927).

[4] Z. anorg. allgem. Chem., **176**, 64 (1928).

[5] Z. anorg. allgem. Chem. **136**, 406 (1904).

[6] Biochem. Z., **147**, 7 (1924).

In connection with the stability of indicator solutions Thiel and Springemann[9] showed that various indicators fade when exposed to light in the presence of organic solvents. Some faded samples regained their color on standing. Brightman and others[10] made a spectrophotometric study of the end point and fading of phenolsulfonphthalein indicators. Marsh[11] found that indicator solutions react with the bottles in which they may be stored, while Schlegel and Steuber[3] recommended keeping the solutions in Pyrex flasks, or coating ordinary glass with paraffin or wax.

Experimental Data

Preparation of Materials. In purifying the materials used and in preparing the solutions the usual precautions for careful work were observed, such as using "conductivity water," recrystallizing salts three times, preserving solutions in Pyrex containers, and adhering to Clark's directions[12] in preparing buffer solutions. The latter were made from the stock solutions just before use.

In addition to regular commercial material, intended for use as indicators, samples of methyl orange[1] and methyl red[13] were purified according to methods given in the respective references. Otherwise the other indicators were used as purchased, since most individuals probably use them in this form, both because various authors so recommend and because of a natural hesitancy to purify materials retailing at their present price. In this case also it was of particular interest to ascertain whether different samples were equally good. Most of the indicators were purchased from such reputable firms as the National Aniline Company, Coleman and Bell, Hynson, Wescott and Dunning, the LaMotte Chemical Company, and the J. T. Baker Chemical Company, each of whom stated that they prepared their own products. In this data reference to the source of each indicator used was purposely omitted since it is not the object of the paper to advertise any concern's product. In case of any marked variations among the results for several different products one should use this particular indicator with suspicion. Most of the indicators were purchased shortly before use, but a few had been in stock at least five years before the solutions were prepared. In some cases the solid indicators from the several manufacturers appeared much alike; in others there was a marked difference in the colors, little of which was observable, however, when the solutions were prepared.

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[7] "Indicators," 92, 183, 184 (1926).

[8] "Determination of Hydrogen Ions", 95 (1927).

[9] Z. anorg. allgem. Chem., **176**, 112 (1928).

[10] J. Am. Chem. Soc., **40**, 1940 (1918).

[11] Science, **59**, 216 (1924).

[12] "Determination of Hydrogen Ions", 192 (1927).

[13] Desvergnes; Ann. chim. anal. chim. appl., **2**, 209, (1920).

Stock solutions of the indicators were prepared by several different methods. One tenth percent aqueous solutions of methyl orange were used throughout, as recommended by Kolthoff.[14] Two hundredths percent solutions of methyl red in 60 percent ethanol were prepared according to Coleman and Bell's directions.[15] Tropaolin OO was prepared in 0.1 percent aqueous solutions,[16] and in 0.1 percent solutions in 50 percent ethanol.[15] The recommendation of Coleman and Bell[15] was followed in preparing a 0.02 percent solution of cresolphthalein in 95 percent ethanol. Three types of solutions were used for the indicators of Clark and Lubs: (1) aqueous solutions prepared according to Clark's directions[16] by adding definite amounts of sodium hydroxide to 0.1 g. of the indicator and diluting to 250 ml.; (2) alcoholic solutions made by dissolving 0.1 g. of the indicator in 52 ml. of neutral 95 percent ethanol, adding the amount of sodium hydroxide specified by Clark, and diluting with water according to Taub's procedure[17]; and (3) according to Kolthoff[14] by dissolving 0.1 g. of the solid in 50 ml. of 95 percent ethanol and diluting with water to 250 ml. With the exceptions noted, Clark's directions were followed in preparing solutions for the comparison of the different products and for the determination of the effect of ultraviolet radiation; likewise, a single product was used in testing different methods of preparation and in preparing the solution for exposure to ultraviolet radiation.

With the exception of tropaolin OO, a sample of each indicator was exposed for two hours to a quartz mercury lamp (Cooper-Hewitt type, designed for operation at four amperes and 220 volts) by placing a thin layer of the solid on a glass about 30 cm. from the lamp. Solutions were then prepared similar to those for the unexposed samples.

Determination of Color. Observations of the various lots of the different indicators, in solutions of different kinds, prepared before and after exposure to ultraviolet radiation, were made by means of a Keuffel and Esser color analyzer (Model C). The procedure followed differed from that reported in an earlier paper[18] only in the use of two 400 w. Mazda lamps for illumination of the samples in the five cm. tubes.

Solutions for the determination of the spectral transmission curves were prepared by diluting one ml. of the stock solutions to 50 ml. with appropriate buffer solutions. Most of the buffers selected were 0.2 pH unit beyond the limits of the useful range of the indicators in order to insure a practically complete conversion to either the basic or acidic color. One sample of each solution so prepared, except tropaolin OO, was exposed in a quartz container to the same conditions of ultraviolet radiation as were the solids.

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[14] "Indicators", 63, 64, 72 (1926).

[15] "Catalog and Price List", 68 (1928).

[16] "Determination of Hydrogen Ions", 94 (1927).

[17] J. Am. Pharm. Assocn., **16**, 118 (1927).

[18] Mellon and Martin: J. Phys. Chem., **31**, 161 (1927).

The data obtained are plotted on a semilogarithmic basis using the percent transmittancy as ordinates and the wave length in millimicrons as abscissas. All of the curves for a given indicator, except thymol blue, are on the same graph. The point used in locating the position of the curves at each interval of ten millimicrons represents the average of five readings on the color analyzer. Of the fourteen indicators studied the curves for cresolphthalein

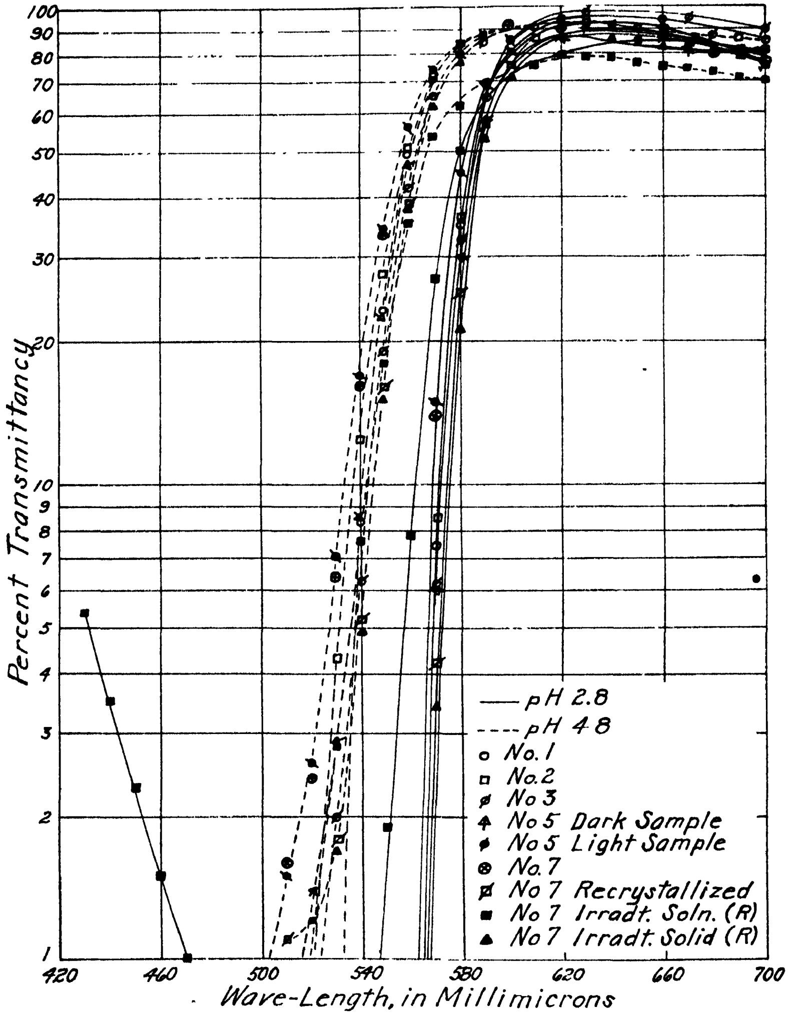

FIG. 1

METHYL ORANGE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.1 percent solution to 50 ml. with a buffer solution.

alone have been omitted since they checked each other so closely. On all the graphs a given number of curve, as No. 1, refers to the product of the same manufacturer.

It may be mentioned that similar spectral transmission curves have already been published[19,4,5,9] for individual samples of practically all of the indicators studied, but in these cases the object was not to determine spectrophotometrically differences of color.

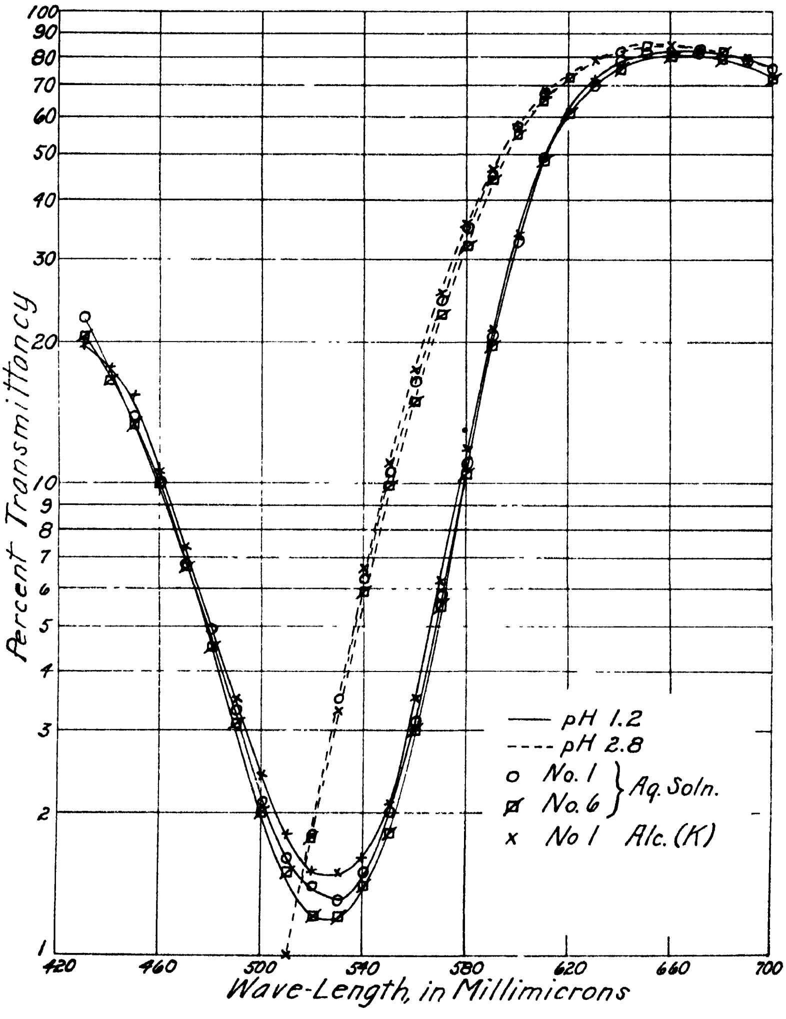

FIG. 2

TROPAOLIN OO. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.1 percent solution to 50 ml. with a buffer solution.

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[19] Brode: J. Am. Chem. Soc., **46**, 581 (1924); Mellon and Martin: Ref. 18; Baker and Davidson: Phot. J., **62**, 375 (1922); Gibbs and Shapiro: J. Am. Chem. Soc., **50**, 2798 (1928).

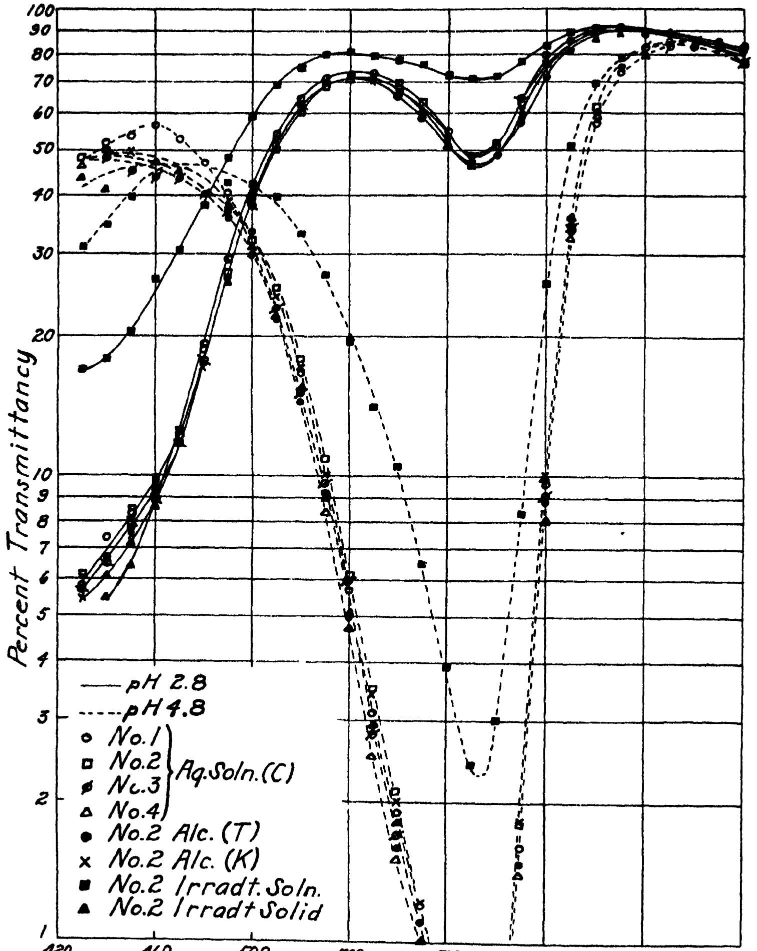

Fig. 3

BROM PHENOL BLUE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 per cent solution to 50 ml. with a buffer solution.

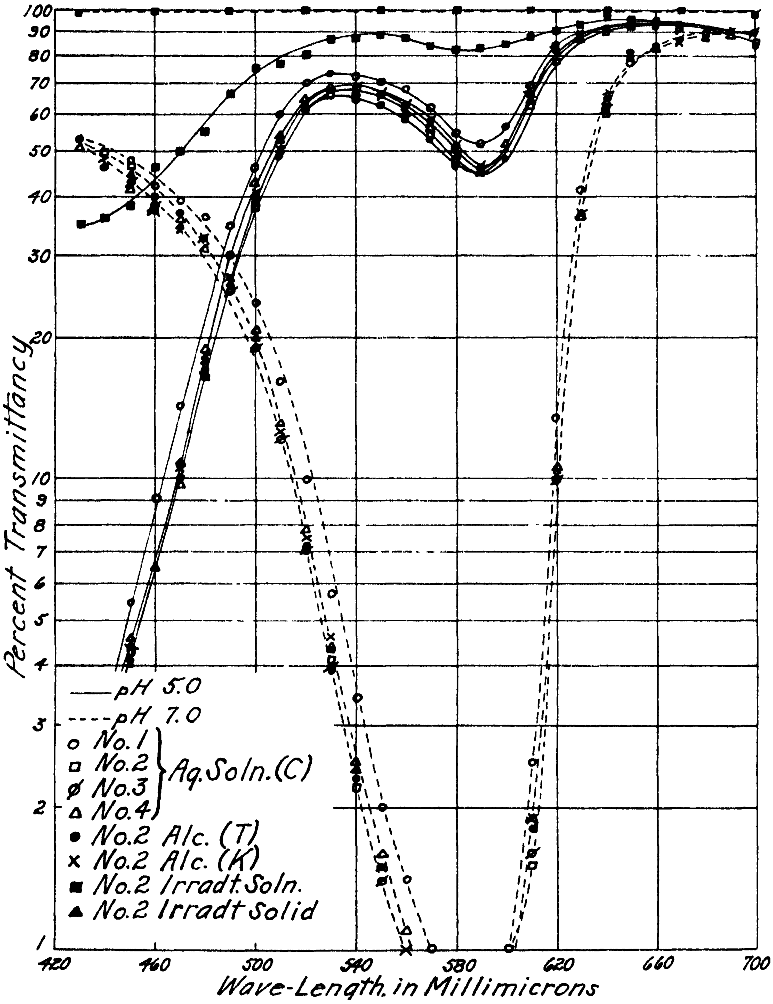

FIG. 4

BROM CRESOL PURPLE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

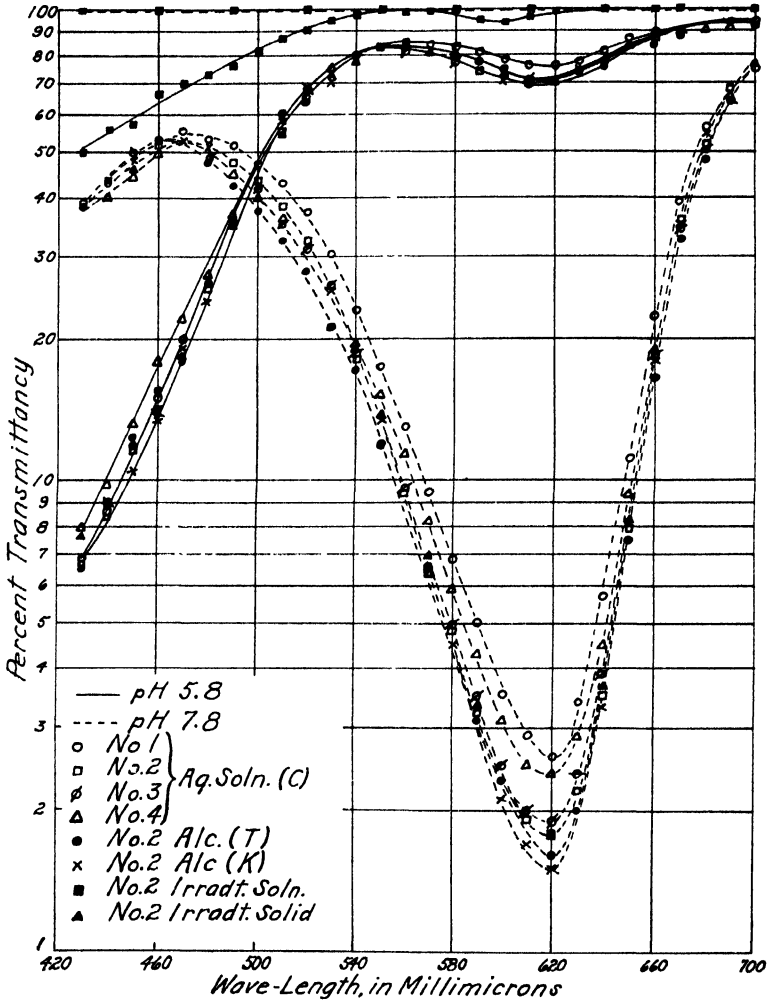

FIG. 5

BROM THYMOL BLUE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

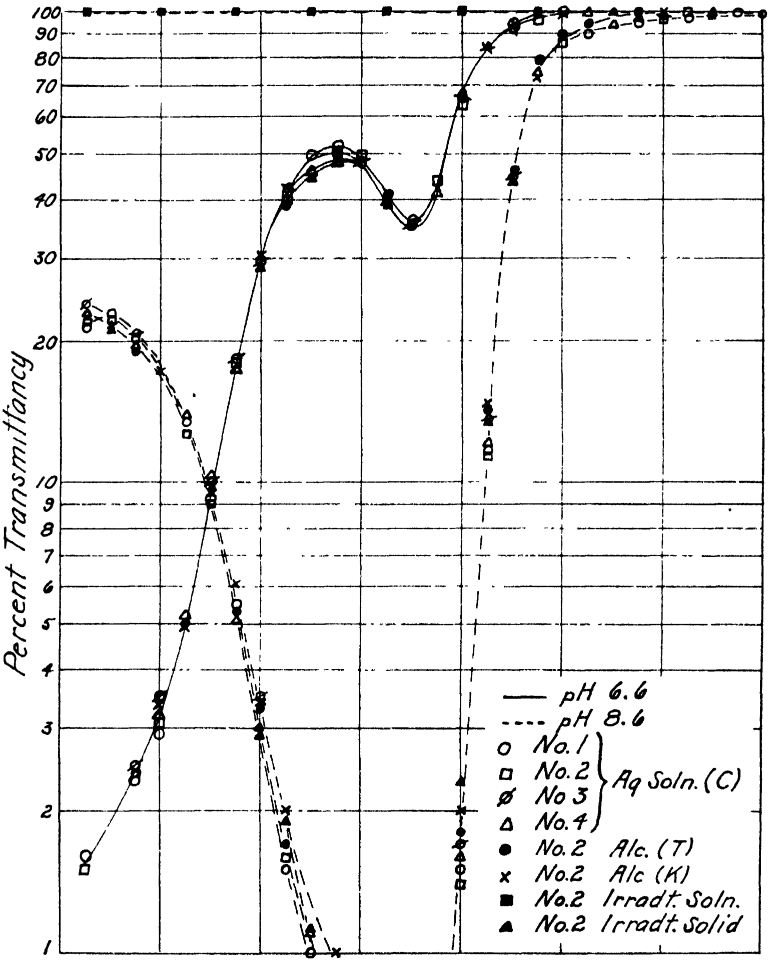

Fig. 6

PHENOL RED. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

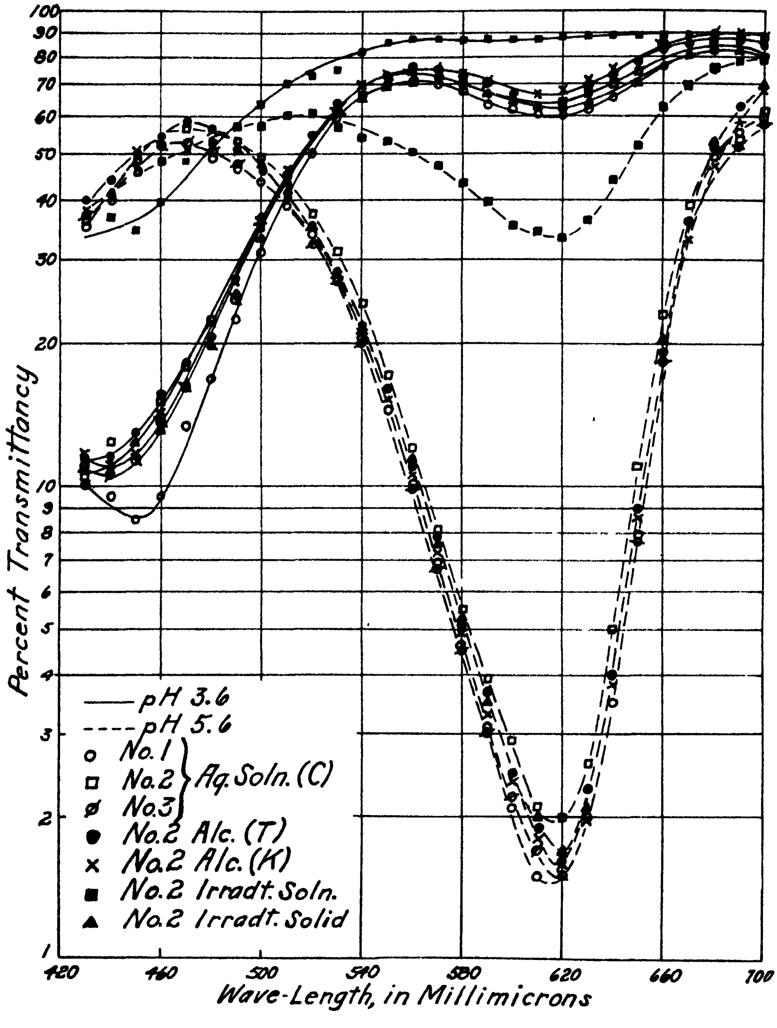

FIG. 7

BROM CRESOL GREEN. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

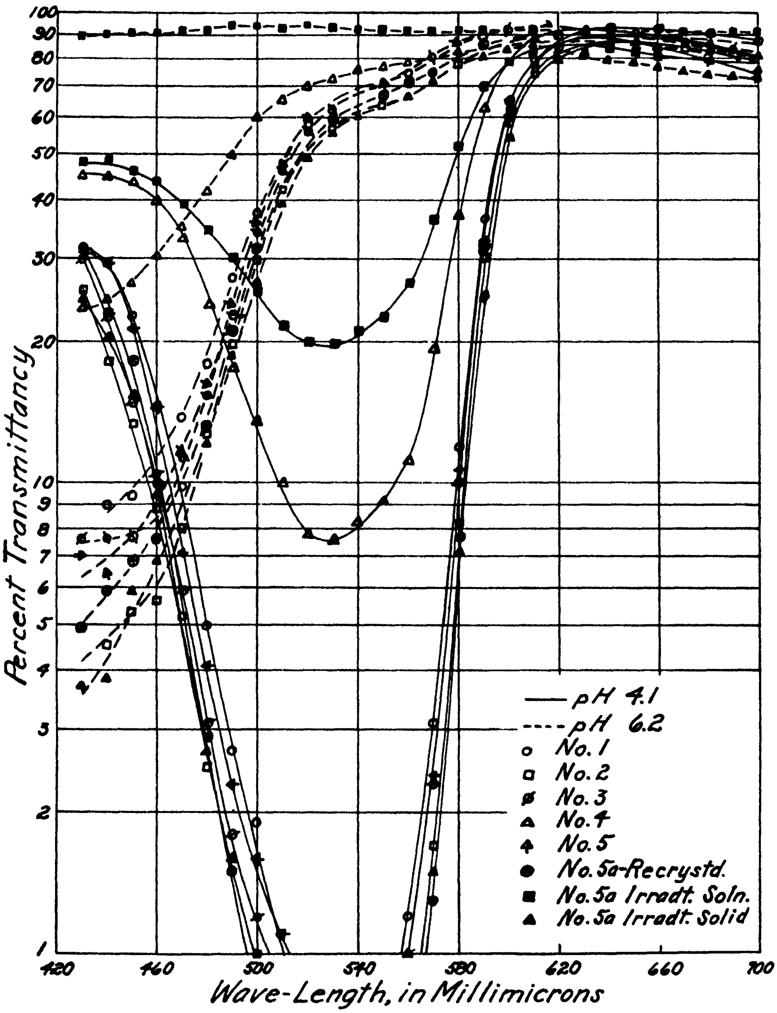

FIG. 8

METHYL RED. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.02 percent solution to 50 ml. with a buffer solution.

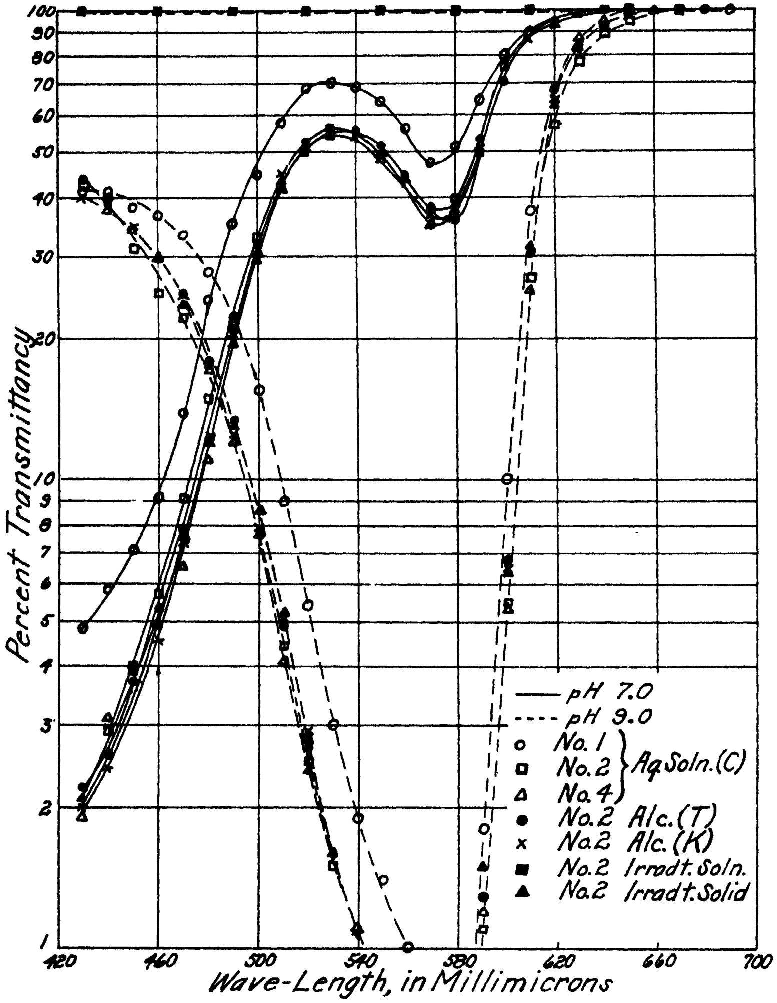

FIG. 9

CRESOL RED. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

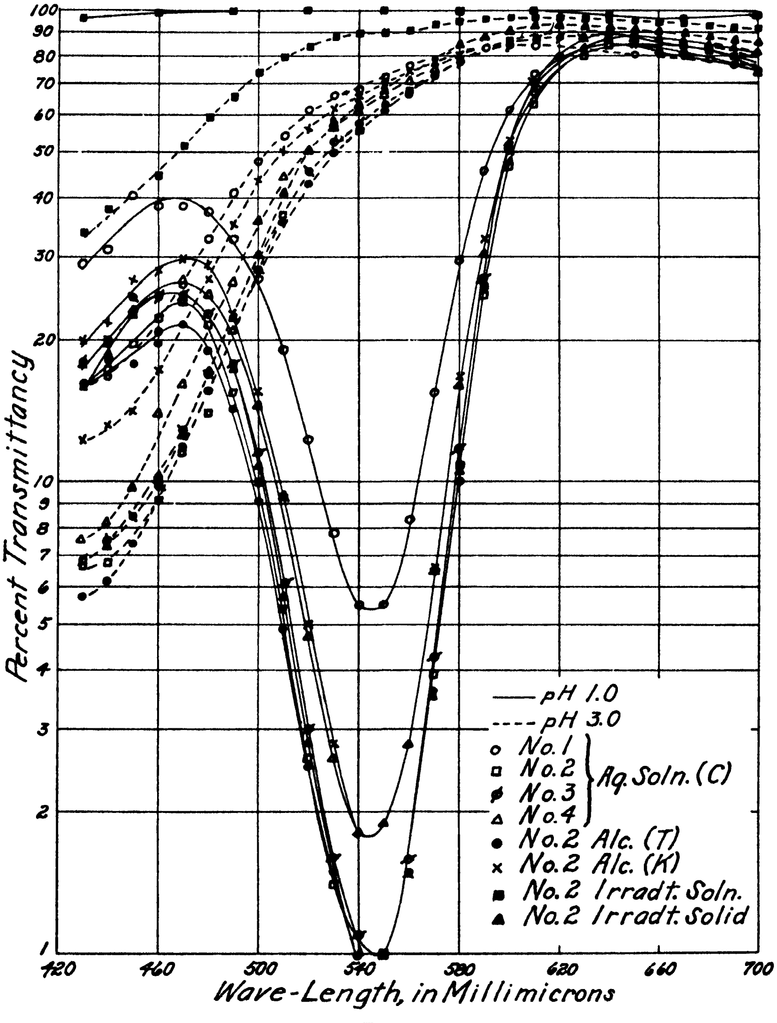

FIG. 10

THYMOL BLUE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

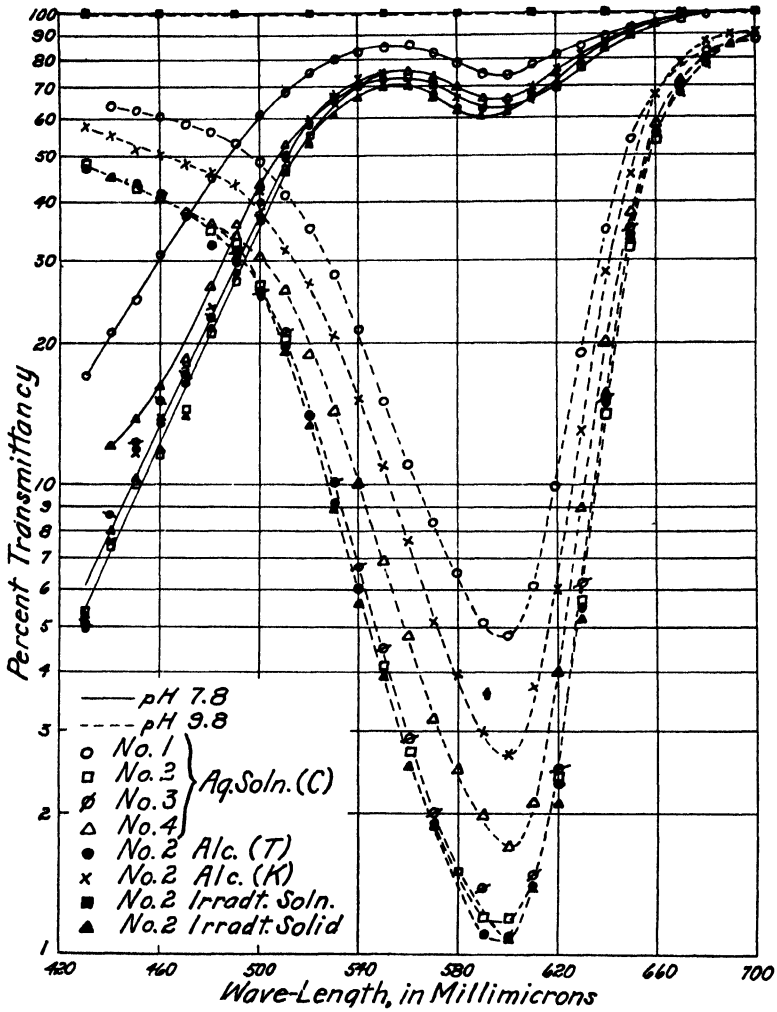

FIG. 11

THYMOL BLUE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 per-cent solution to 50 ml. with a buffer solution.

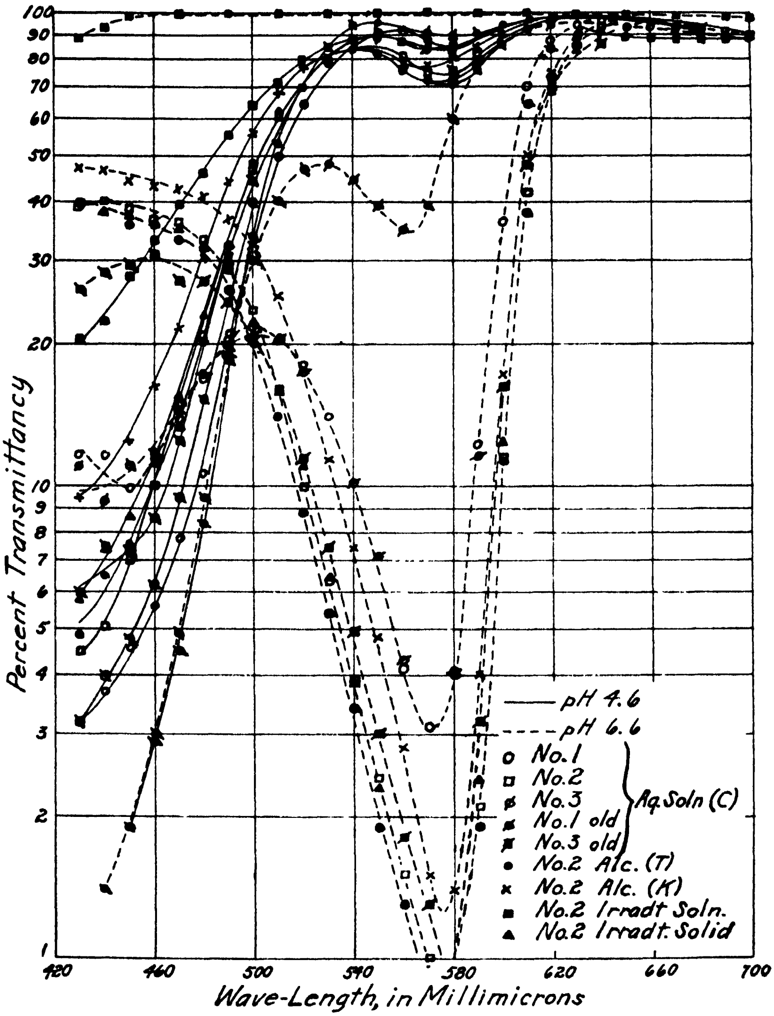

Fig. 12

CHLOR PHENOL RED. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

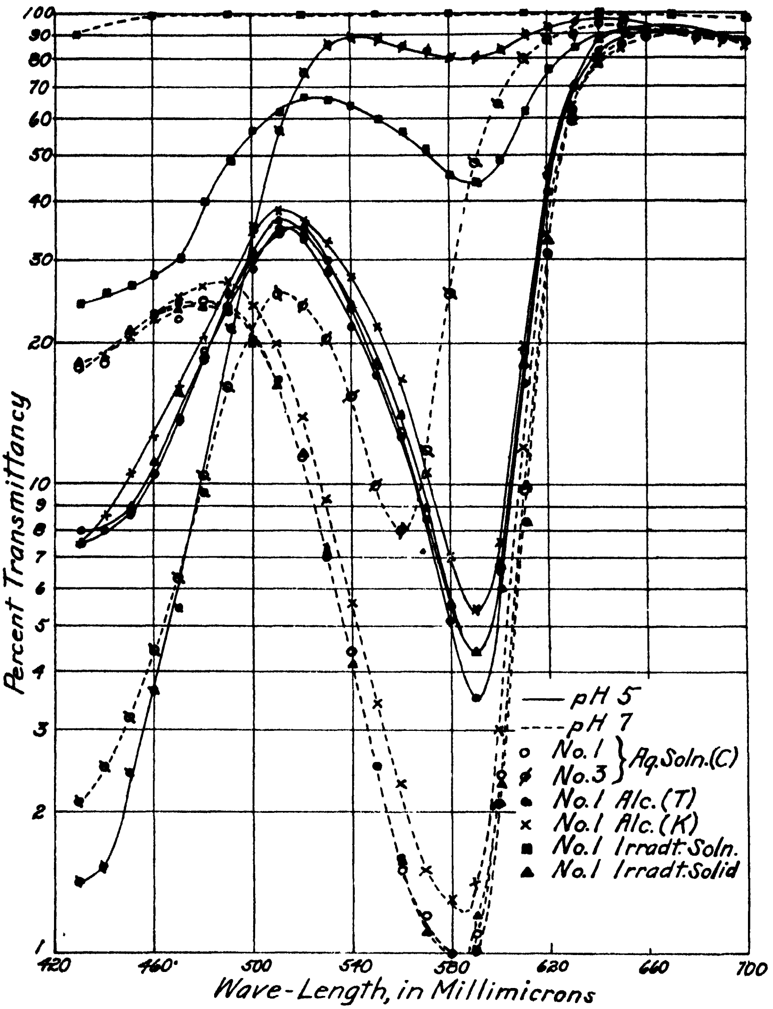

FIG. 13

BROM PHENOL RED. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

Discussion

For the purpose of the present investigation it seemed that curves coordinating transmittancy and wave length would be of most value as a basis for formulating conclusions. If two solutions, for example, yield curves practically superimposable upon each other, within the limits obtainable with the spectrophotometer used, one may conclude that the samples exhibit the same color. But if there is a marked divergence between the curves for two different solutions, this fact in itself is definite evidence of divergence in the colorimetric characteristics of the two systems. Obviously, the spectrophotometric curves show merely whether there is a difference between samples; where a difference is found little direct evidence is provided to indicate the cause.

Having in mind that our present interest is in the divergence of the curves for any given indicator, we may consider the data from the view point of several different factors thought to be of possible significance in connection with the use of indicator solutions. These factors are discussed separately below.

Effect of Ultraviolet Radiation. The chief visible effect of ultraviolet radiation on the solid indicators was to cause considerable darkening during exposure of brom phenol blue, brom cresol green, brom cresol purple, and brom thymol blue. Solutions of the exposed solids gave curves which were practically identical with those for the solutions of the unexposed solids. Any differences of appearance of the irradiated solids did not extend to the hue of the solutions. In view of the effect on the solutions, however, perhaps a longer exposure would have produced more significant results.

Fading, varying from an almost negligible amount to a complete disappearance of hue, occurred in all of the solutions which were exposed to ultraviolet radiation. Absence of color would indicate the destruction in the solution of whatever had been functioning in the system as a selective absorber of visual radiation. Such effects raise the question of the possible action of sunlight on any solutions found to be sensitive to ultraviolet radiation.

Effect of the Method of preparing the Solutions. From a study of the curves it is evident that differences in the method of preparing the indicator solutions had no appreciable effect in the case of tropaolin OO, brom phenol blue, brom cresol green, brom cresol purple, brom thymol blue, phenol red and cresol red. Only one kind of solution was used for methyl orange, methyl red and cresolphthalein.

For the remaining indicators the curves obtained for the different solutions varied more or less. In most cases the solutions prepared according to Taub's method compare quite favorably with those prepared following Clark's directions. Those prepared according to Kolthoff's suggestion varied to a greater or less extent from those prepared by the other two methods. From the curve it would seem that the small amount of alcohol used in preparing the solutions made no appreciable difference in the color. It is a question whether the variations in the solutions prepared by Kolthoff's method were due to the absence of sodium hydroxide in the stock solutions or to the presence of alcohol. Since the solutions prepared by Taub's method contained alcohol and agreed fairly well with those prepared by Clark's method, it is reasonable to assume that the differences are connected with the neutralization of the indicator in preparing the solutions, rather than with the presence of the alcohol.

Effect of the Source of the Indicators. The appearance of the solid indicators from the different sources varied considerably. While these differences were quite marked, they did not extend to the solutions; in fact, some of the solids appearing most nearly alike showed the greatest variation in their spectral transmission curves.

The curves for the different samples of methyl orange, tropaolin OO, brom phenol blue, brom cresol green, brom cresol purple, phenol red, and cresolphthalein, compare quite favorably with each other. The small variations in these indicators would probably be of no significance in the colorimetric determination of pH values. The remaining indicators, presenting variations more or less marked, are considered individually.

For methyl red the agreement was fairly good with the exception of one old sample (more than five years) and of the region of shorter wave lengths at pH 6.2.

For thymol blue, at both sets of pH values, two samples stand out as being different in color. One of these (No. 4) was an old sample.

The curves for chlor phenol red show the widest variation, especially at the higher pH value and for one old sample (No. 1). Qualitative tests on this sample showed its pH range to be approximately 6.4 to 7.6 instead of the normal range of 4.8 to 6.4. Thus, the hue of the solution was still yellow at a pH value where it should have been fully red*.

The two available samples of brom phenol red, one of which was old (No. 1), gave curves quite different from each other. In connection with this indicator, as also with chlor red phenol, it may be mentioned that the manufacturer of the old sample stated it is their belief that results, such as those encountered with chlor phenol red, may be due to a decomposition of the indicator or to an incomplete halogenation at the time of preparing the solid material. In the present instance the old sample of chlor phenol red was not showing its normal transformation range at the time of purchase.

For brom thymol blue the chief variation occurred, curiously, at the minimum point for the higher pH value.

For cresol red one sample stands out as having a high transmittancy. In all such cases it may be kept in mind that a high transmittancy means that the solution is absorbing less visible radiation and hence may be referred to as being paler or having a higher relative brilliance. Presumably such a solution contains a smaller concentration of the selective absorber due to the lower degree of purity of the solid indicator.

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* Harden has just published [J. Am. Chem. Soc., 52, 4611 (1930)] a note regarding variations in different samples of chlor phenol red.

Summary and Conclusions

As a result of the foregoing spectrophotometric study of certain indicators, it may be concluded, on the basis of the curves obtained, that the source of the compounds, the method of preparing their solutions, and the action of ultraviolet radiation upon the latter are all of more or less significance in affecting the color of the solutions. These effects vary with the different compounds, but in general the actions may be summarized as follows:

1. The decolorizing effect of ultraviolet radiation on buffer solutions of indicators shows their photochemical sensitivity. In view of this action, and of the change in hue of some of the solids on irradiation, such systems probably should be protected from strong sources of photochemically active radiant energy.

2. Differences in the method of preparing the indicator solutions may have an observable effect upon the hue obtained. It would seem advisable, therefore, to specify a uniform method of preparing such solutions whenever any variation would be liable to produce significant variations in the results obtained with the use of the indicator.

3. Indicators from different sources may show considerable variation in the color of their solutions. Whatever may be its cause, the fact of this variation's occurrence makes necessary a careful inspection of any sample intended for use wherever the several attributes of color, hue, relative brilliance, and colorimetric purity, must have definite values, as in the possible preparation of permanent colorimetric standards to match indicator solutions. For any work of this kind indicators should meet definite specifications.

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THE DECOMPOSITION OF DIETHYL ETHER IN CONTACT WITH PLATINUM AND TUNGSTEN

BY H. AUSTIN TAYLOR AND M. SCHWARTZ[1]

The recent theories that have been suggested to account for the existence of homogeneous unimolecular gas reactions have as their basic principle the fact that the loss of activated molecules due to reaction must be compensated for in one way or another. The number of active molecules must of necessity be a constant fraction of the reactant concentration for the reaction to be of first order. If the temperature of the reactant as a whole be raised, a point may be reached where the Maxwellian distribution will provide active molecules at a rate sufficient to allow reaction to proceed with a measurable velocity. Alternatively, it should be possible to supply this necessary concentration of active molecules in an atmosphere, otherwise relatively cold, by furnishing a source from which molecules could absorb energy, for example by collision with a heated filament.

Such a condition would appear the more probable if the view first suggested by Lindemann[2] to account for unimolecular reactions be adopted. On this view the molecule may become activated by collision with other molecules but possesses a mean life before reaction. Such a condition would be favored by complexity of the molecule since energy may then be stored in a large number of degrees of freedom. Complex molecules therefore would appear to be able to maintain rheit necessary energy above the average for some time after the instant of having received it, whatever the actual mechanism of the reception may have been.

Under the conditions postulated then, the reaction would appear to be homogeneous, that is, independent of the material forming the filament and would be of the same order and possess the same energy of activation as the reaction studied under the more normal conditions of higher temperature throughout the gas as a whole. Such would appear to be the explanation of the decomposition of acetone in contact with platinum recently studied by one of us.[3]

It should be emphasised at this stage that the above conditions must not be confused with those obtaining in typical heterogeneous reactions where a definite adsorption for a period of time must be postulated. Even the rather exceptional heterogeneous decomposition of nitrous oxide in contact with gold which Hinshelwood[4] has shown may be accounted for on the assumption that nearly every molecule striking the wire decomposes, is entirely different. In this reaction, the homogeneous decomposition is bimolecular with an energy of activation of 58,500 calories per two moles, whilst on platinum and gold the reactions are of first order with energies of 32,500 and 29,000 calories respectively. In the acetone decomposition the energy of activation was the same in the truly homogeneous reaction as in the presence of the heated filament, the apparently heterogeneous condition.

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[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] Trans. Faraday Soc., **17**, 598 (1922).

[3] Taylor: J. Phys. Chem., **33**, 1793 (1929).

[4] Proc. Roy. Soc., **108A**, 211 (1925).

The possibility of distinguishing between the two methods of obtaining the necessary concentration of active molecules, and at the same time actually confirming the correctness of the mechanism here suggested, presents itself in the existence of reactions whose velocities studied under the more usual conditions fall off as the pressure is decreased. The rate of production of active molecules by collision then becomes less than their rate of decomposition and the reaction is no longer unimolecular. Activation by a heated filament would not suffer from this peculiarity until probably much later in the course of the reaction or at much lower pressures. Unfortunately the decomposition of acetone has not been studied at low pressure so that a test of the above could not be applied in that case. For that reason the decomposition of diethyl ether was studied in the above manner since it has been found[1] that below a pressure of about 150 mms. the velocity constant falls considerably, it being anticipated that no falling off would be observed under the changed conditions until much lower pressures were reached.

The apparatus and method of procedure was similar to that described in the previous work on acetone. The manometer and capillary connecting tubes were maintained at a temperature above the boiling point of the ether, whilst the reaction vessel was immersed in a thermostat at 35°C.

Measurements were made at four different temperatures using various initial pressures of ether. The total pressure increase obtained during the reaction at the various temperatures are shown in Table I.

TABLE I

Temp. ° C.	$\frac{\text{Total increase}}{\text{Initial pressure}}$	Temp. ° C..	$\frac{\text{Total increase}}{\text{Initial pressure}}$
846	2.17	942	2 42
892	2.34	968	2.45

The ratios are slightly larger than those observed by Hinshelwood but actually are closer to the 2.5 ratio to be expected on the basis of the assumed mode of decomposition.

$$C_2H_5OC_2H_5 = 2CH_4 + 1/2\ C_2H_4 + CO$$

In all probability then the decomposition is the same as that in the homogeneous reaction. Table II gives the times in minutes observed for 25, 50 and 75 percent decomposition.

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[1] Hinshelwood: Proc. Roy. Soc., **114A**, 84 (1927).

TABLE II

Initial pressure (mms)		t_{25}	t_{50}	t_{75} mins.
A. Temperature 846° C.				
160		3.6	9.8	20.3
171		3.5	9.4	21.5
184		3.5	9.7	23.0
196		3.4	9.5	22.0
205		3.5	9.6	22.5
217		3.4	9.2	21.5
	Mean	3.5	9.5	21.8
B. Temperature 892° C.				
149		1.2	3.2	8.2
160		1.2	3.4	8.3
173		1.2	3.4	8.5
186		1.2	3.3	8.2
196		1.2	3.2	8.0
206		1.2	3.2	8.0
	Mean	1.2	3.3	8.2
C. Temperature 942° C.				
142		.43	1.1	2.8
153		.42	1.2	2.8
165		.45	1.2	2.9
177		.43	1.2	3.0
192		.46	1.2	2.9
199		.42	1.1	2.8
	Mean	.44	1.2	2.9
D. Temperature 968° C.				
134		.27	.70	1.8
146		.26	.69	1.7
157		.25	.69	1.7
173		.25	.68	1.6
186		.26	.66	1.6
196		.27	.64	1.5
	Mean	.26	.68	1.7

The obvious constancy of these times over the pressure range studied is ample evidence of the unimolecular nature of the reaction. The constancy of the three-quarter life is especially remarkable, and would suggest that a constant value would be obtained for calculations of the velocity constant. Table III shows the results obtained in a typical determination.

TABLE III

Temperature 846° C. Initial Pressure 205 mms.

Time (mins)	Pressure Increase (mms)	k	Time (mins)	Pressure Increase (mms)	k
1	39	.0919	25	347	.0609
2	71	.0872	30	368	0588
3	99	.0842	35	382	.0563
4	123	.0811	40	395	.0551
5	145	.0791	50	412	0526
7	183	.0759	60	425	0525
10	229	.0726	70	435	0549
15	284	.0681	80	442	.0675
20	321	0642			

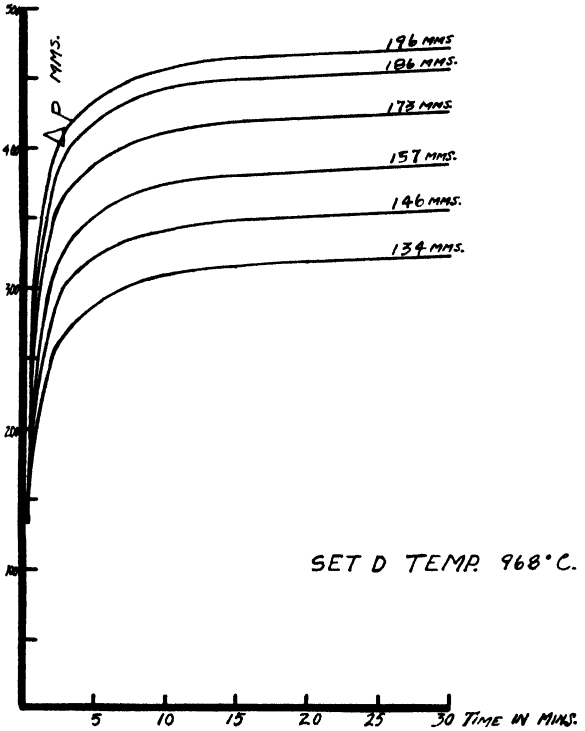

FIG. 1

The value of k the unimolecular velocity constant, it will be observed, falls steadily as the reaction proceeds, even in the first few minutes of reaction. One might be tempted to account for this on the basis that the reaction was deviating from its unimolecular nature as the reactant concentration decreased. In view however of the constancy of the three-quarter life such an explanation is hardly tenable. What appears more probable is that the reaction is not a simple one but is probably composed of two simultaneous unimolecular reactions each with its own velocity constant. Such might account also for the deviation observed between the total pressure increase and that theoretically to be expected.

The results obtained for the rate of pressure increase with time are shown in a typical case in Fig. 1.

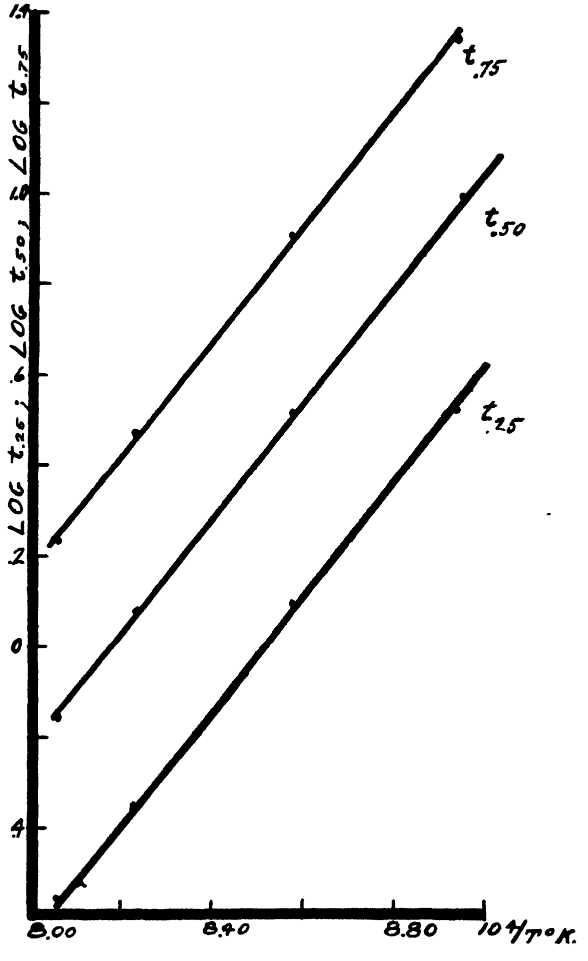

FIG. 2

The calculation of the heat of activation from the times of quarter, half and three-quarter decomposition give the results shown in Table IV.

TABLE IV

Sets	Energy of Activation from t_{25}	t_{50}	t_{75}
A-B	58,200	58,200	54,000
B-C	57,250	57,250	58,500
C-D	55,100	59,900	55,100

Fig. 2 shows the straight lines obtained by plotting the logarithm of the time against the reciprocal of the absolute temperature. The average energy of activation is 57,000 calories which is at least of the same order of magnitude as that obtained by Hinshelwood namely 53,000. The difference however would appear to be outside the limits of experimental error. In order to determine therefore whether this deviation was due in any way to the presence of platinum in the system the experiments were repeated using a tungsten filament. It was found that the results were not as reproducible with tungsten as with platinum since experience showed that if the tungsten filament was allowed to glow during evacuation of the reaction vessel marked evaporation of tungsten occurred and the characteristics of the wire changed considerably. It was necessary then to evacuate with the filament cold and probably therefore the surface conditions were not as reproducible as in the case of platinum since it must be remembered that carbon monoxide is one of the products of decomposition.

Measurements were again made at four different temperatures. The tungsten was of approximately the same diameter as the platinum previously used, the temperatures with tungsten being higher than with platinum for a given speed of reaction.

Table V gives the times for 25, 50 and 75 percent decomposition.

TABLE V

E. Temperature 915° C.		t_{25}	t_{50}	t_{75} (mins)
157		3.0	9.3	21.5
170		3.2	9.3	22.0
182		3.2	9.7	22.7
	Mean	3.1	9.4	22.1
F. Temperature 934° C.				
172		2.0	6.4	15.5
184		1.9	6.3	15.9
208		2.1	7.1*	17.5*
221		2.2	7.2*	17.0*
185		1.7*	6.3	15.5
	Mean	2.1	6.3	15.7
G. Temperature 953° C.				
160		1.2	4.2	10.8
176		1.3	4.3	11.1
182		1.3	4.3	11.0
195		1.3	4.5	11.5
	Mean	1.3	4.3	11.1
H. Temperature 973° C.				
159		.95	2.4	6.2
170		.89	2.8	7.5
184		.88	2.9	8.0
193		.92	2.9	8.0
	Mean	.91	2.8	7.8

* Not included.

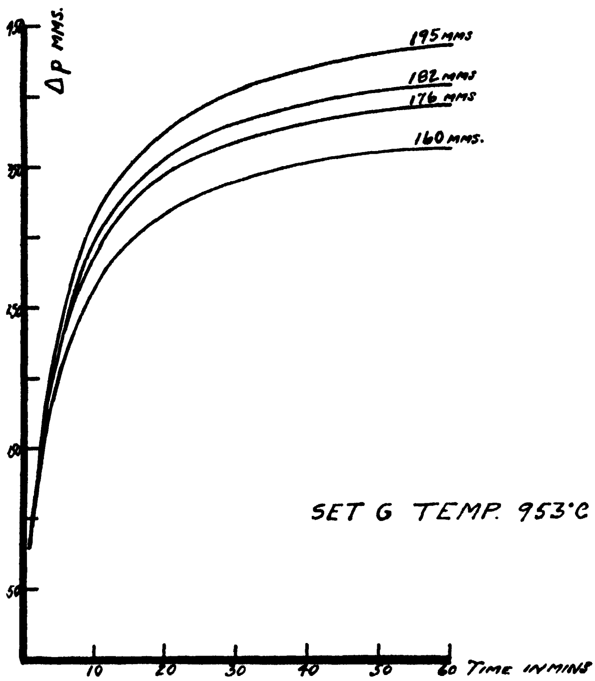

FIG. 3

The reaction again therefore is unimolecular. The velocity constants as in the case of platinum likewise exhibit a similar steady falling trend, shown in Table VI.

TABLE VI

Temperature 915° C. Initial Pressure 157 mms

Time (mins)	Pressure Increase (mms)	k
1	43	.134
2	67	.109
3	86	097
4	102	089
5	118	.085
7	147	.080
10	179	074
15	220	.069
20	250	066
25	270	.062
30	285	.060
40	305	.056
50	319	.054
60	328	.053
70	335	.056

No comparison can be made naturally between the actual values of the constants in the two cases of platinum and tungsten since each will depend on the specific dimensions of the apparatus. That the reaction however is probably the same in both cases may be seen from the similarity of the ratios of total pressure increase to initial pressure for tungsten as in Table VII, and those for platinum previously given.

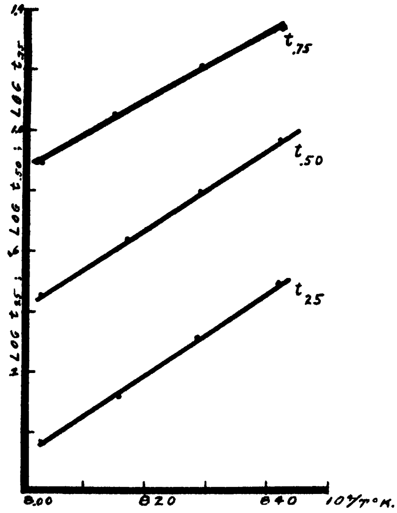

Fig. 4

TABLE VII

Temp. °C.	Total increase / Initial pressure	Temp. °C.	Total increase / Initial pressure
915	2.15	953	2.25
934	2.23	973	2 31

Fig. 3 gives a typical example of the pressure increase-time curves obtained using tungsten.

The calculation of the heat of activation from the times of 25, 50 and 75 percent decomposition as made previously for platinum gives an average value of 58,000 calories for tungsten as against 57,000 for platinum. The plot of the logarithm of the times against temperature is shown in Fig. 4.

There can be no doubt therefore that the reaction in presence of the heated filaments is truly homogeneous. The temperatures used were chosen so that the observed rate of reaction would be of the same order as those found by Hinshelwood, and it will be noted that there is no deviation from unimolecularity in the neighborhood of 150 mms. and in fact down to 100 mms.

This does not preclude the possibility that the constant might fall at still lower pressures or as Hinshelwood has shown, at comparable pressures when the total reaction rate is slower, that is, at lower temperatures.

The fact that the energies of activation for platinum and tungsten are in such good agreement is significant. Whether the discrepancy between the average value 57,000 calories here obtained and the 53,000 previously quoted is significant, cannot definitely be said. Judging from the change in the calculated energy of activation caused by an error of only five seconds in the time of 25 percent decomposition, the discrepancy would appear to be within the limits of error at least for tungsten where the reproducibility was not so good as for platinum.

TABLE VIII

Temperature °C.	Time for 50 percent pressure increase mins.	Heat of Activation
	Bulb No. 2.	
825	6.5	
800	11.0	49,300
775	17.8	43,100
750	28.6	40,500
725	76	79,400
700	164	59,400
	Bulb No. 1 secs.	
800	58	
750	192	52,300
700	585	44,000

There exists however the possibility that under the conditions used a molecule having become activated by collision with or proximity to the hot filament might, in passing into the colder atmosphere in the reaction bulb, radiate some of its energy. Such a molecule would require to absorb an energy greater than the critical energy in order that it should still have the necessary activation at the end of its active life before decomposition.

During the preparation of the manuscript for the above paper the authors[1] called our attention to a similar research. Their conclusions are in agreement with ours although their particular apparatus has allowed them to realise the deviation from unimolecularity at higher pressure. The energy of activation, 52,000 calories, obtained graphically by them would seem to be in closer agreement with Hinshelwood's value than ours. If however the values for the various temperature intervals are calculated separately the agreement is seen to be fortuitous. Table VIII gives these values in detail.

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[1] Steacie and Campbell: Proc. Roy. Soc., **128A**, 451 (1930).

It is obvious therefore that no particular stress can be laid on the absolute value of the energy term.

Summary

The decomposition of diethyl ether in presence of heated filaments of both platinum and tungsten has been shown to be identical with the ordinary homogeneous reaction. The presence of the filament serves merely to furnish the necessary stationary concentration of active molecules.

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THE ENERGY DIAGRAM OF SODIUM CHLORIDE

BY PIERRE J. VAN RYSSELBERGE

Introduction

In recent times, under the influence of various theories and experimental facts, such as the Lewis theory of valence, the results of the X-ray analysis of crystals, the properties of electrolytes, etc., it has been customary to consider salts of the type of sodium chloride as polar compounds. In such compounds the bond existing between the two constituents consists mainly of the electrical attraction of two oppositely charged ions. A crystal of sodium chloride is considered as a purely ionic lattice, in which the various ions are held together at definite distances from one another in a certain geometrical pattern because of the interplay of two kinds of forces: the Coulomb electrical forces and the Born repulsive forces of which the wave mechanics of Schrödinger has recently given an interpretation.[1] In solution, such a crystal dissociates into free ions which in dilute solutions obey, with a fairly good approximation, the laws of the Debye-Hückel theory of electrolytes. Departure from these laws has been explained by Bjerrum[2] as due to partial physical association. Using Bjerrum's terminology,[3] we say that a crystal of sodium chloride is completely ionized but also completely "associated" and that aqueous solutions of sodium chloride are completely ionized but partially "associated," or clustered.

Nernst and his co-workers,[4] on the basis of measurements of heats of dilution of strong electrolytes, were able to determine directly the degrees of association and the heat involved in the dissociation into single ions of those associated groups (Na-Cl, for instance) which if we choose to we may call neutral molecules. In order to explain these results it was found necessary to modify the Debye-Hückel theory in a fundamental way. The fact that the degrees of association found by Nernst and the resulting dissociation constants explain rather well the properties of mixtures of potassium and sodium chlorides[5] makes it plausible to suppose that in such solutions we are dealing with actual neutral molecules in which a pair of electrons is shared between the two atoms.

The existence of individual molecules of the alkali halides in the vapor state is obvious as shown for instance by the discussion of the photochemical decomposition of these molecules by Kistiakowsky.[6]

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[1] L. Pauling: J. Am. Chem. Soc., 49, 765 (1927); A. Sommerfeld: "Atombau und Spektrallinien. Wellenmechanischer Ergänzungsband," p. 116 (1929).

[2] N. Bjerrum: Det. Kgl. danske Vidensk. selskab. Math-fys. Medd., VII, No. 9 (1926).

[3] N. Bjerrum: Ber., 62B, 1091 (1929).

[4] W. Nernst: Z. physik. Chem., 135, 237 (1928).

[5] J. W. McBain and P. J. Van Rysselberge: J. Am. Chem. Soc., 52, 2336 (1930).

[6] G. B. Kistiakowsky: "Photochemical Processes," p. 31 (1928).

London[1] gives a method of deciding whether a compound is polar or homopolar. The expression

$$\Phi = E_{\infty} - \frac{z_+ \, z_- \, e^2}{r} \qquad (1)$$

represents the potential energy of the system of two ions (Na^+ and Cl^- for instance) for large values of r. E_{∞} is the sum of the ionization energy of the cation and of the electroaffinity of the anion. z_+ and z_- are the valences of the two ions, e the elementary charge, r the distance between the centers of the ions.

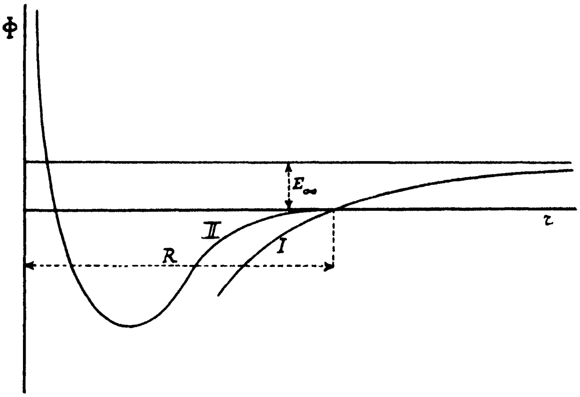

FIG. 1

For Φ = 0 we have:

$$R = \frac{z_+ \, z_- \, e^2}{E_{\infty}} \qquad (2)$$

If we express E_{∞} in volt electrons we obtain:

$$R = \frac{z_+ \, z_- \times 14.3}{E_{\infty}} \text{ Å} \qquad (3)$$

The potential energy for the system of neutral atoms passes through a minimum, then coincides very rapidly with the horizontal axis. This is a generalization of the consequences of the theory of Heitler and London[2] explaining the formation of a molecule of hydrogen from two neutral atoms, on the basis of the perturbation theory of wave mechanics.

At the distance R given by equation (3) the curves corresponding to the ions (polar curve), I, and the one corresponding to the neutral atoms, II, intersect each other as shown on Fig. 1.

According to London, we have the following criterion: if the distance R is much larger than the known distance between two oppositely charged ions in the crystal, the compound is polar; if R is of the order of magnitude of the distance between the atoms in the molecule, the compound is homopolar.

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[1] F. London: Z. Physik, **46**, 455 (1927).

[2] W. Heitler and F. London: Z. Physik, **44**, 455 (1927).

London found, for instance, that hydrogen halides are probably homopolar, a conclusion already drawn by Franck,[1] and that alkali halides are decidedly polar. Another test to determine whether a compound is polar or non-polar is given by Pauling[2]: "if the internuclear equilibrium distance calculated for a polar structure with the aid of the known properties of ions agrees with the value found from experiment, the molecule is polar; the equilibrium distance for a shared electron bond would, on the other hand, be smaller than that calculated."

Williams[3] suggests that a compound like sodium chloride exists under two forms: a purely polar one and a homopolar one having a structure analogous to that of a hydrogen molecule, in which a pair of electrons with opposite spins is shared between the two atoms. According to the state (vapor, crystal or solution) of sodium chloride, variable amounts of both types of molecules are present. Such a picture would replace the idea of continuous transition from the homopolar to the polar bond, often proposed by chemists.

In the presence of these new ideas and of the rather uncertain views about the nature of chemical bonds, it seemed useful and important to us to determine a complete interaction energy diagram for sodium chloride, using trustworthy data on ionization potential, electroaffinity, heat of dissociation in the vapor state and in solution, crystal structure, etc. Such a diagram, besides being a novelty, brings into light a few interesting facts, as we proceed to show.

II. Gaseous Ions, Dissolved Ions. Ionization Potential, Electroaffinity

The difference between gaseous ions and dissolved ions has been clearly explained by Fredenhagen.[4] If we call dissolution energy the one corresponding to the transformation of a dissolved ion into a gaseous atom, ionization energy the one corresponding to the transformation of a gaseous atom into a gaseous ion, and solvation energy the one corresponding to the transformation of a dissolved ion into a gaseous ion, the following relation must hold[5]:

dissolution energy + ionization energy = solvation energy
dissolved ion gaseous atom dissolved ion
→gaseous atom →gaseous ion →gaseous ion

The dissolution energies should not be confused with the normal electrode potentials. The dissolution energy corresponds to the transformation of one gas atom into a dissolved ion, when the concentrations of the atoms in the gas phase and of the ions in the solution are equal.

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[1] J. Franck, H. Kuhn, and G. Rollefson: Z. Physik, **43**, 155; J. Franck and H. Kuhn: 169 (1927).

[2] L. Pauling: Proc. Nat. Acad. Sci., **14**, 359 (1928).

[3] A. T. Williams: Physik. Z., **31**, 367 (1930).

[4] K. Fredenhagen: Z. physik. Chem., **128**, 1, 239 (1927); **134**, 33 (1928); **140**, 65; **140**, 435; **141**, 195 (1929).

[5] See specially: K. Fredenhagen: Z. physik. Chem., **140**, 69 and seq. (1929).

In the case of Na and Cl, we have the energy relationships given by Fig. 2. 5.13 V. is the ionization potential of sodium, 3.7 V. is the electroaffinity of chlorine. If we consider as a reference energy that corresponding to a system composed of neutral sodium and chlorine atoms in the gaseous state, the system gaseous Na^+ + gaeous Cl^- will have an energy content of:

$$5.13 - 3.70 = +1.43 \text{ V. e.}$$

The system dissolved Na^+ + dissolved Cl^- will have an energy content of:

$$-(3.49 + 2.46) = -5.94 \text{ V.e,}$$

according to the dissolution energies given by Fredenhagen.[1]

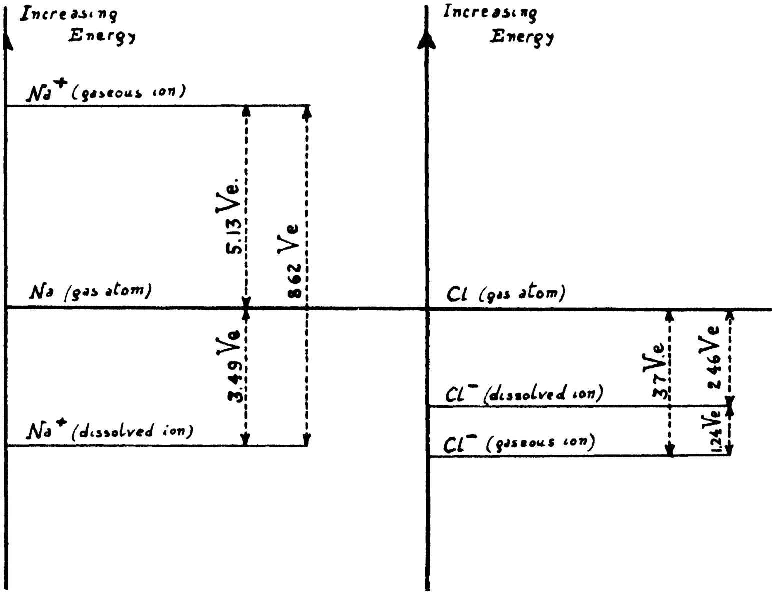

FIG. 2

On Fig. 3 where the interaction potential energy is plotted against the distance between the sodium and chlorine nuclei, the horizontal line at +1.43 V. from the level 0 is asymptotic to the interaction curve of the gaseous ionic system, I. In the same way the horizontal line at 5.95 V.e. below the level 0 is asymptotic to the interaction curve of the dissolved ionic system.

III. Interaction Curve for the Gaseous Ionic System

The interaction energy between the two gaseous ions is given by

$$\Phi = E_\infty - \frac{e^2}{r} + \frac{B}{r^n} \tag{4}$$

in which E_∞ is the sum of the ionization energy of sodium and of the electroaffinity of chlorine, $-e^2/r$ is the potential energy due to the Coulomb forces and B/r^n is the potential energy due to the Born repulsive forces. At large distances $\Phi = E_\infty$; at moderate distances the term B/r^n is negligible; at very small distances Φ passes through a minimum corresponding to the equilibrium distance between the Na^+ and Cl^- ions.

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[1] K. Fredenhagen: Z. physik. Chem., **140**, 71 (1929).

Taking the derivative of Φ with regard to r and equating it to 0, we find:

$$B = e^2 \cdot \frac{R^{n-1}}{n} \tag{5}$$

R being the equilibrium distance.

(4) becomes, for $r = R$:

$$\Phi = E_\infty - \frac{e^2}{R}\left(1 - \frac{1}{n}\right) \tag{6}$$

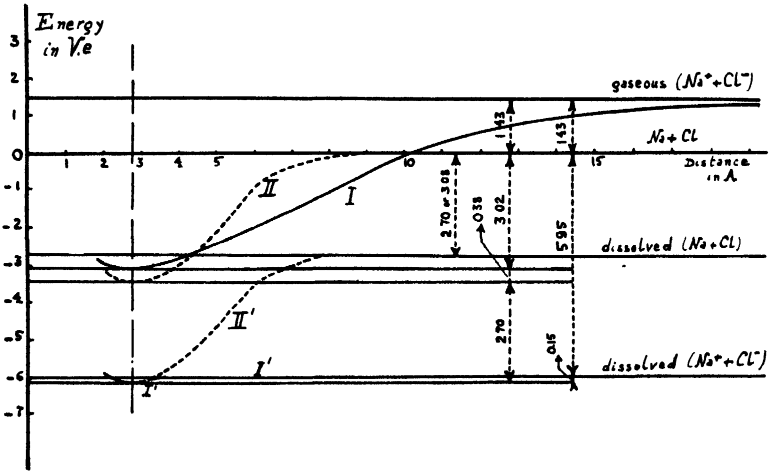

FIG. 3

For sodium chloride, we have as shown in the preceding section $E_\infty = 1.43$ V.e. Taking for R and n the values given by Pauling[1] for the NaCl crystal, i.e. $R = 2.81$ Å and $n = 8$, we obtain:

$$\Phi_{\text{min.}} = 1.43 - \frac{14.3}{2.81}\left(1 - \frac{1}{8}\right) = -3.02 \text{ V.e.} \tag{7}$$

The complete curve for the system (gaseous Na^+ + gaseous Cl^-), I, can then be drawn easily (Fig. 3). It cuts the horizontal axis at $r = 10$ Å.

Fredenhagen[2] on the basis of numerical data given in the Landolt-Börnstein tables and of computations of von Wartenberg[3] gives for the dissociation energy of gaseous NaCl into gaseous Na and Cl: 78,500 calories which corresponds to -3.40 V.e. On account of the small accuracy of such a figure, we may consider this value as practically identical with that of the minimum in the interaction of the ionic system (-3.02 V.e.). This result seems to show that the bond in gaseous NaCl is polar. It is unfortunately impossible to compute the interaction curve for neutral atoms of Na and Cl, i.e. the curve corresponding to a hypothetical homopolar bond. We may draw such a curve in an approximate way if we suppose that the minimum in the interaction curve of the gaseous system might correspond to a homopolar bond: the appearance of the curve would be that of the upper dotted line II in Fig. 3.

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[1] L. Pauling: J. Am. Chem. Soc., **49**, 765 (1927).

[2] K. Fredenhagen: Z. physik. Chem., **134**, 38 (1928).

[3] H. von Wartenberg: Z. anorg. Chem., **151**, 328 (1926).

IV. Interaction Curve for the Dissolved Ionic System

The Coulomb potential in the case of an aqueous solution is very small. It means that the interaction curve for the dissolved Na^+ and Cl^- ions is practically identical with the horizontal line at -5.95 V.e. from the 0 level down to quite small distances.

Let us suppose that, if Na^+ and Cl^- form a neutral molecule or a physical aggregate or cluster in Bjerrum's sense, the equilibrium distance between the two constituents is the same as in the NaCl crystal, i.e., 2.81 Å.

For this particular value of r the interaction curve will present a minimum which we can determine from the value given by Nernst[1] for the dissociation energy of the molecule or physical aggregate NaCl: 3,500 calories per mole. This dissociation energy corresponds to 0.15 V.e. The minimum is then at 0.15 V.e. below the horizontal line of the dissolved Na^+ and Cl^- ions, as shown in Fig. 3, curve I′.

We notice that the two minima, the one corresponding to the gaseous state and the one corresponding to the dissolved NaCl are 2.70.V.e. apart. If we consider the calculated minimum of the upper curve as more accurate, those minima are 3.08 V.e. apart. Supposing that this difference of energy content is the one corresponding to the purely hypothetical process gaseous (Na + Cl) →dissolved (Na + Cl), we may draw an horizontal line at 3.08 V.e. below the 0-level. In case the minimum in the interaction curve of the system dissolved Na^+ + dissolved Cl^- corresponds to a homopolar molecule, the interaction curve for the system dissolved Na+ dissolved Cl has the form of the lower dotted line II′ on Fig. 3.

In aqueous solution, the system ($Na^+ + Cl^-$) corresponds to a much lower energy content than the neutral system: it is the stable one. For small distances between the ions, small amounts of molecules (or physical aggregates?) are formed.

In the case of the gaseous state the curves for the neutral and the ionic systems intersect each other in two points. There is a marked tendency to dissociation of sodium chloride into neutral atoms, a fact which allows us to suppose that the molecule may possess a homopolar character.

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[1] W. Nernst: loc. cit.

V. Summary

1. Current ideas about the structure of compounds of the type of sodium chloride have been reviewed.

2. Curves representing the interaction energy of sodium and chlorine ions and atoms in the gaseous state and in solution in terms of the distance between the nuclei of the two constituents have been drawn.

3. The resulting energy diagram has been discussed.

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THE SURFACE CHEMISTRY OF HYDRATES. I

Aged Hydrous Alumina*

BY V. R. DAMERELL

Introduction

When hydrous aluminum oxide, precipitated with ammonium hydroxide from cold solution, has been allowed to age under water for several months at room temperature, and then dried in the air, a substance of doubtful nature has resulted. It has long been thought that this air-dried product might be a definite hydrate, since it approximately corresponds to a trihydrate in composition;[1] but when examined by the usual methods of hydrate analysis it has failed to show the characteristics of one with any clearness. Thus when dried over various hydrates and desiccants its water content takes a different and nearly always meaningless value for each. The drying curve of Hüttig and von Wittgenstein[2] gives no exact information in the case of their preparation, B_2. Unfortunately they did not take enough low temperature readings to show the course of the curve at the trihydrate stage. Guichard[3] obtained a slight break in the water content-temperature curve when he heated the substance obtained at ordinary temperature, which had dried in the air for six months, using a method of weight change with constantly increasing temperature, but this break is difficult to interpret accurately. Furthermore, he showed that heating had a marked effect on the substance, as shown by the entirely different curve obtained using a preparation that had been boiled in water. For this reason there is doubt whether any of the hydrates claimed by Willstätter[4] are identical with the one in question, since some heating was used in all of his preparations. Also the continuous drying curve of Shidei[5] may have been of another substance, since a hot dialysis was used in the purification of his preparation.

However, by experimenting with precipitates containing particles of different average size, there has been obtained evidence of the true composition of the substance, and of its surface behaviour under different vapor pressures.

Let W_s be the total number of molecules of water, both adsorbed and chemically combined, present for each molecule of aluminum oxide in a small particle precipitate, and W_l be the total number in a large particle precipitate. Let C be the total number of molecules chemically combined, and A_s and A_l the total number adsorbed in each case. Making the reasonable assumption that C is the same for all sizes of particles, under the same conditions,

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* Contribution from the Morley Chemical Laboratory of Western Reserve University.

[1] Tommasi: Compt. rend., **91**, 231 (1880); van Bemmelen: Rec. Trav. chim., **7**, 75 (1888); cf. J. Chem. Soc., **53A**, 1159 (1888).

[2] Z. anorg. Chem., **171**, 323 (1928).

[3] Bull., **37**, 62 (1925).

[4] Ber., **58**, 2448, 2458 (1925); **57**, 58, 1082 (1924); **56**, 149 (1923).

[5] Mem. Coll. Sci. Kyoto, **9a**, 42 (1924); cf. Chem. Abs., **20**, 684 (1926).

$$(1) \quad W_s - C = A_s$$

$$(2) \quad W_l - C = A_l$$

Let S_s and S_l be the total accessible surfaces of the small and large particle precipitates respectively, each of which contains the same number of molecules of aluminum oxide. If the particles are of such size and shape, and are so arranged that the space between does not, as a whole, become congested with water molecules at a given vapor pressure and temperature, then the following should be true, at least as a close approximation.

$$(3) \quad \frac{A_s}{A_l} = \frac{S_s}{S_l} \quad \text{and,}$$

$$(4) \quad \frac{W_s - C}{W_l - C} = \frac{S_s}{S_l}$$

If two precipitates containing particles of different average size are allowed to stand together over one hydrate until maximum adsorption, or the same fraction of maximum adsorption has taken place in each case, and if this be repeated over a second hydrate, always choosing such vapor pressures that the space between particles does not become congested with water, then if C remains the same for both vapor pressures, the following results from (4)

$$(5) \quad \left[\frac{W_s - C}{W_l - C}\right] \begin{array}{l}\text{over first}\\ \text{hydrate}\end{array} = \left[\frac{W_s' - C}{W_l' - C}\right] \begin{array}{l}\text{over second}\\ \text{hydrate}\end{array}$$

since if C remains the same, assuming no change of crystalline form, the total surfaces should not alter. Small temperature changes should not seriously affect this equality, as long as both grades of precipitates are treated just alike regarding these variations, time of standing, and as long as C remains constant.

As a test of this equation (5) it should be possible to obtain values for W experimentally, and then substitute various values for C until an equality resulted. If this value were close to a small whole number, and if a number of pairs of precipitates, each containing a different average size of particle, gave essentially this value, it would constitute good evidence that the substance under investigation was a definite hydrate, that C had remained constant, and that the above assumptions were correct.

The object of this investigation was (a) to determine whether aged hydrous aluminum oxide was a definite hydrate, and (b) to study the surface behaviour of this substance when allowed to stand over compounds having different water vapor pressures, using the method outlined above.

Experimental

Preparation of different grades of precipitates.

A kilogram of recrystallized aluminum sulfate ($Al_2(SO_4)_3.18H_2O$) was dissolved in twenty liters of cold distilled water, and a small excess of a solution of distilled ammonia was added at once with vigorous stirring, the mixing taking place at room temperature. The resulting precipitate was allowed to settle a day or so and then the supernatant liquid was removed by means of a syphon. It was found that a glass tube bent up at the end could be used very effectively for this purpose, with practically no loss of precipitate. After syphoning, distilled water was added with stirring and the precipitate allowed to settle again. It was washed in this way at intervals of one or two days for six weeks, all washings being done at room temperature. Small amounts of ammonia were added occasionally during the first washings, to help in removing the sulfate. At the end of six weeks washing was discontinued, since the precipitate had become peptized. Samples were then dissolved in acid, and tested in the usual qualitative manner for ammonia and sulfate. No sulfate could be detected, and the ratio of equivalents of ammonia to equivalents of alumina was about one to six hundred.

In order to separate this precipitate into portions containing particles of a different average size, it was suspended by vigorous stirring and then allowed to stand for about twenty minutes, when a layer of larger particles settled to the bottom of the container. The suspension above this settled layer was syphoned off to another container and allowed to stand for an hour or so, during which time a layer of smaller particles settled out. This process was repeated a third time in one experiment, several days being allowed for the finest layer to form. These different grades of precipitates were separated from some excess water by filtering on fine-pored filter paper, and were allowed to dry in the air for several weeks. The air-dried precipitates were the starting products for a series of water vapor adsorption experiments. All of the precipitates had stood under water from two to three months before this final separation and air drying took place.

Water Adsorption Experiments.

The precipitates took the form of small, very porous lumps when air dried, and were left this way during the desiccator experiments. They were transferred to large weighing bottles, 2.75 inches in diameter and 1.25 inches deep, with ground glass covers. Large samples were taken (10 to 20 grams) to decrease the experimental error. Two series of water adsorption experiments were completed. In the first, two air-dried precipitates were allowed to stand in succession over phosphorus pentoxide, the partially dehydrated monohydrate of sodium carbonate, and the partially dehydrated heptahydrate of the same substance. The precipitates contained a different average size of particle, and were designated as large and small particle precipitates respectively. (See Pair I, Tables II and III). In the second experiment three precipitates of different average particle size, designated as large, small and very small, respectively, were allowed to stand in succession over the partially dehydrated monohydrate of sodium carbonate, the partially dehydrated heptahydrate, and phosphorus pentoxide. (See Pairs II, III and IV, Tables II and III).

It was not considered necessary to wait for complete constancy of weight at the various vapor pressures, since to obtain absolute equilibrium required considerable time, and maximum gain or loss of water was not particularly desired. When the change in weight became less than one part per thousand, during a period of forty-eight hours, it was assumed that the fraction of maximum gain or loss was essentially the same for each precipitate. The experiments were carried out in a constant temperature room, with an observed temperature of 23° ± 1°C. As proof of the assumption that the fraction of maximum loss or gain of water was essentially the same for each precipitate at the time that weighing was stopped, it was noticed in every case that the ratio between weight gained or lost by each precipitate during the last few weighings was nearly constant, as shown in Table I.

TABLE I

Water lost by air-dried precipitates standing over the partially dehydrated monohydrate of sodium carbonate

grams of air dried precipitate	size of particle	hours between weighing	192	43	49	56	44	48
22.981	large	loss of weight	224	19	16	18	13	4
13.159	small	between each weighing	173	22	15	18	11	3
11.161	very small	in milligrams	187	17	16	19	13	4

Gain or loss of water threatened to take place very rapidly when the desiccators were opened, so the procedure adopted was to put the ground-glass covers on the weighing bottles immediately upon removing the desiccator cover, and then to weigh them as rapidly as possible. Since the gain or loss of weight was slow from the covered weighing bottles, this source of error was small.

The water content of the precipitates was finally determined by transferring them to weighed platinum crucibles and igniting to constant weight. The precipitates, when first dried, after being filtered, left a film on the glass which was difficult to remove quantitatively. For this reason they were not dried originally in the weighing bottles, but on large watch glasses, and were transferred to the weighing bottles after becoming dry. By doing this, it later became easy to transfer the precipitates from the weighing bottles to the crucibles in a quantitative manner.

The water content assumed by each precipitate under different vapor pressures is given in Table II, and the values for C which satisfy equation (5) for the various pairs are given in Table III.

TABLE II

Water content, in parts per 100 parts of aluminum oxide, assumed by each precipitate over phosphorus pentoxide, and the mono and hepta hydrate of sodium carbonate

Experiment	pair	size of particle	over P_2O_5		over $Na_2Co_3 1H_2O$		over $Na_2CO_3 7H_2O$	
			water content	side from which equilibrium was approached	water content	side from which equilibrium was approached	water content	side from which equilibrium was approached
First	I	small	49.44	above	53.83	below	61.18	below
		large	50.98	above	53.63	below	57.64	below
Second	II	very small	50.97	above	56.92	above	60.38	below
		small	51.93	above	56.63	above	59.39	below
”	III	very small	50.97	above	56.92	above	60.38	below
		large	52.74	above	55.92	above	57.85	below
”	IV	small	51.93	above	56.63	above	59.39	below
		large	52.74	above	55.92	above	57.85	below

TABLE III

Values for C which satisfy equation (5) for each pair of precipitates and each pair of vapor pressure sources

Pair	over $\begin{cases} P_2O_5 \\ Na_2CO_3.1H_2O \end{cases}$	over $\begin{cases} Na_2CO_3.1H_2O \\ Na_2CO_3.7H_2O \end{cases}$	over $\begin{cases} P_2O_5 \\ Na_2CO_3.7H_2O \end{cases}$
I	3.02	3.02	3.00
II	3.15	3.15	3.15
III	3.11	3.10	3.11
IV	3.09	3.08	3.09

Discussion of Results

Many modern investigators consider that there is no fundamental difference between the force involved in a chemical bond and in the binding which holds an adsorbed molecule.[6] In discussing the results given above, however, both terms will be retained, since the work largely deals with surfaces. Thus water which is attracted to or leaves the particles in an amount proportional to the surface will be designated as adsorbed water, while water which is present in a stoichiometrical ratio to the amount of aluminum oxide will be designated as chemically bound water.

Since definite values for C were able to be obtained which were close to three, it is concluded that the substance is a definite trihydrate of alumina, and not aluminum oxide and adsorbed water, as Shidei[7] concluded after study of a somewhat similar system. In view of the work of Pascal,[8] on the magnetic susceptibilities of various alumina preparations, and because of its ready loss of water, the substance will be referred to as a trihydrate and not as aluminum hydroxide.

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[6] Cf. Langmuir: J. Am. Chem. Soc., **38**, 2225 (1916).

[7] Mem. Coll. Sci. Kyoto, **9a**, 42 (1924); cf. Chem. Abs., **20**, 684 (1926).

[8] Compt. rend., **178**, 481 (1924).

As the results in Table III show, the average value for C is several per cent higher than that required for the trihydrate. This can be accounted for by assuming the presence of other types of adsorbed water, such as water held jointly by two surfaces, which were not considered in the derivation of (5). The presence of water adsorbed by two or more surfaces is very probable, and should become a factor of more importance as the particle size became smaller.

When the hydrate was allowed to stand over phosphorus pentoxide, an interesting surface phenomenon took place. Part of the water which the positive adsorption experiments had indicated as being chemically bound now apparently behaved as adsorbed water, escaping in proportion to the surface. Thus if the loss be considered as negative adsorption, with the surface of the particles becoming 'pitted', $(W_s-C)/(W_1-C)$ can be calculated for various values of C. When C is larger than W, both parts of the fraction become negative, but the quotient remains positive, and the values can be compared with those for positive adsorption. The values which satisfy equation (5) for various pairs are given in the first and last columns of table III, and it is seen that they are very similar to the values in the middle column from the positive adsorption experiments.

The picture indicated by these results is one of a precipitate containing a great number of very small, probably crystalline particles, whose total surface must be very large. Additional water can be held on the surfaces of these particles, which has the property of adsorbed water, since at a given vapor pressure its quantity varies with the surface. When the vapor pressure becomes low enough, part of the water in the surface of the hydrate particles, which was apparently chemically combined during higher vapor pressures, now behaves as adsorbed water, leaving in an amount proportional to the hydrate surface. The relation between this surface decomposition and the constant vapor pressure decomposition of hydrates is being made the object of further study. It is very probable that this escape of water in proportion to the surface is the initial step in the decomposition mechanism.

Simon and Fischer,[9] in repeating an experiment of Hagiwara,[10] found that the composition of dried hydrargillite was essentially that required for the trihydrate, but that the same substance, ground to a very fine powder with quartz sand, when dried at the same temperature, analyzed to be Al_2O_3 $2.78H_2O$. They attributed their results to local heating during the grinding. From the results obtained in this laboratory, with a substance which is either the same, or closely related to hydrargillite, it is concluded that the difference in water content which Simon and Fischer observed was not due primarily to local heating, but was probably a natural consequence of the great increase in surface, since similar results were observed by the author with precipitates which had not been subjected to grinding.

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[9] Z. anorg. Chem., **185**, 101 (1929).

[10] Kolloid-Z., **32**, 154 (1923).

Conclusion

1. Experimental evidence has been given showing that hydrous aluminum oxide, when aged under water containing small amounts of ammonia for several months at room temperature, forms a compound with water, which is probably a trihydrate.

2. At room temperature this compound adsorbs water in proportion to its surface when allowed to stand over the partially dehydrated mono and heptahydrate of sodium carbonate.

3. Over phosphorus pentoxide, at room temperature, the hydrate particles lose chemically bound water, which under these conditions behave as adsorbed water and escapes in proportion to the surface.

4. The difference in water content between ground and unground hydrargillite, explained by Simon and Fischer as being due to local heating during the grinding, has been observed in precipitates of a different average size of particle that have not been subjected to grinding, and is probably not primarily due to local heating, but is a natural consequence of the increase in surface.

THE PARTIAL PRESSURES OF VAPOURS OF VOLATILE LIQUIDS IN THE PRESENCE OF INERT GASES[1]

BY W. G. BEARE, G. A. McVICAR AND J. B. FERGUSON[2]

When a volatile liquid is placed in a closed vessel which contains a relatively inert gas and the temperature is kept constant, the partial pressure of the vapour of this liquid is frequently regarded as approximately equal to the difference between the initial gas pressure and the final total pressure; it is considered to differ from this by a negligible amount after corrections are applied for the change in volume of the vapour phase and the loss of permanent gas by solution, provided that the gas phase is a perfect gaseous solution, and that adsorption on the walls of the vessel is not a disturbing factor. The vapour pressure is obtained from the partial pressure by making an allowance for the diminution of the partial pressure caused by the solution of gas in the liquid when this is an appreciable amount.

There does not appear to be any sound theoretical objection to the method outlined for the treatment of the case cited or for similar cases but there is the practical objection, as noted by Dornte,[3] that it is quite at variance with the published results of Regnault[4] and Campbell.[5] Either these results are incorrect or some additional factor must be considered in the theoretical treatment of the case. The matter is of such importance that we felt that the facts in the case should be clearly established. Accordingly, we carried out several series of experiments similar in principle to those of Campbell but essentially different in respect to the apparatus and technique used. Our results, which are given in this paper, do not confirm the results of the earlier experiments.

Materials

Methyl alcohol: Kahlbaum. Dried over freshly prepared lime at room temperature, decanted off and distilled.
D 20/4 0.79232. I.C.T. value 0.7917.
Estimated to be 99.8 percent alcohol.

Ethyl alcohol: Squibbs. Similarly dried.
D 20/4 0.78913. I.C.T. value 0.78934.
Estimated to be pure.

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[1] Presented at the 13th Annual Canadian Chemical Convention held at Ottawa, May 26, 1930.

[2] Measurements by Messrs. Beare and McVicar.

[3] Dornte: J. Phys. Chem., **33**, 1312 (1929).

[4] Regnault: Mém. de Paris, **26**, 679 (1862).

[5] Campbell: Trans. Faraday Soc., **10**, 197 (1914).

Acetone: Kahlbaum, aus der Bisulfit Verbindung. Dried over fused calcium chloride at room temperature, decanted off and distilled.

D 20/4 0.79106. This was not quite dry as the material we prepared last year gave 0.79072.[6]

Ether: Eastman Kodak. This was shaken with clean dry mercury twice, filtered through charcoal, shaken with its own volume of water and the latter operation repeated five times with one-half the quantity of water. The separated product was first dried over fused calcium chloride and then over sodium and distilled.

Air: This was passed through a concentrated aqueous solution of sodium hydroxide, over soda-lime, calcium chloride and phosphorus pentoxide in the order given.

Carbon dioxide: This was prepared by dropping a concentrated aqueous solution of sodium bicarbonate into concentrated sulphuric acid and dried over calcium chloride and phosphorus pentoxide.

Apparatus and Procedure

The apparatus of Ferguson and Funnell[7] as modified by Beare and McVicar[6] together with the additional part, A′, needed for the present work, is shown in Fig. 1. The part, A′, was sealed into the apparatus between the large and the small bulbs in the large air bath. The solenoids of the circulating pump are unfortunately not indicated in their proper positions. Although movable, they were placed close together in actual operation.

A glass container of suitable size was filled with the liquid under investigation, sealed and placed in A′. A trace of lubricant was placed on the ground-glass joint and enough mercury was kept in the glass cap to protect this seal. The apparatus was then evacuated. The air baths were brought up to the desired temperatures, the lower air bath being about four degrees above the temperature at which the vapour pressure was to be determined, the upper about ten degrees above this. If the manometer reading remained constant for several hours or more, the apparatus was considered gas-tight. The gas (air or carbon dioxide) was then admitted until the desired pressure was reached, approximately. Mercury was run into the U tube until it reached a point in the capillary tube just inside of the upper air bath. The temperatures of the air baths were again adjusted, also the height of the mercury column and the pressure reading taken. The container tip was broken with the magnetic hammer; liquid air was placed around the small bulb and the circulating pump started. A small wire heater (not shown) surrounding A′ was turned on and the sample collected in the small bulb. The heater was disconnected, the liquid air removed, the air baths brought up to temperature and cold water circulated through the water bath. When no more of the sample remained as liquid in the small bulb the water bath was heated up and maintained at the desired temperature. This temperature was read on a Beckmann thermometer which had been compared with a standard, was kept constant to ± 0.01°C. and known within ±0.02°C. The temperature of the lower air bath was kept constant to ± 0.1°C. and that of the upper to ± 0.5°C. The pump was run at full speed until the pressure became constant. With air, this required approximately 1.5 hours and with carbon dioxide 2.5 hours. The pressure rose gradually until it attained its maximum value. The pump was kept running at full speed for an additional 0.5 hours, the speed was reduced and finally the pump was stopped but observations were continued for an hour after the stoppage. Reducing the pump speed made no appreciable difference in the pressure reading but the final reading was usually 0.2-0.3 mm lower than the readings with pump operating. This difference we attributed to a heat effect.

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[6] Beare, McVicar and Ferguson: J. Phys. Chem., **34**, 1310 (1930).

[7] Ferguson and Funnell: J. Phys. Chem., **33**, 1 (1929).

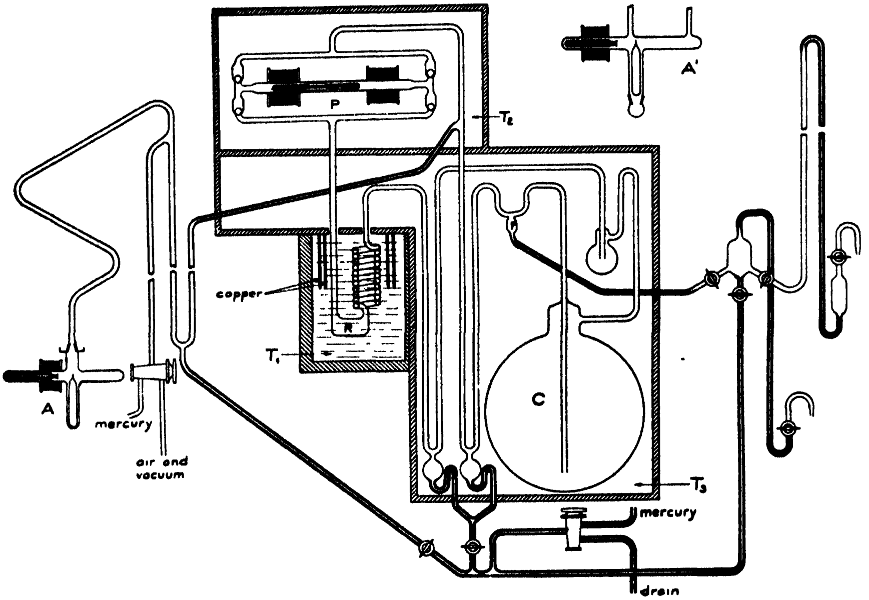

Fig. 1

In experiments, in which air was the inert gas, the small bulb was again cooled with liquid air, the pump operated and the sample collected in this bulb. The apparatus was then evacuated, closed by the mercury column and the vapour pressure of the liquid determined. The details need not be repeated for this operation.

The difference between the initial gas pressure and the final pressure was taken as the approximate partial pressure. All pressure readings were reduced to 0°C. Allowance was then made for the following experimental conditions:

(a). The initial temperature of the reaction chamber which had a volume of 15 cc. was not always identical with its temperature when the final pressure reading was taken.

(b). The evaporation of the liquid increased the volume of the gas phase.

(c). Part of the inert gas dissolved in the liquid phase, the volume of which was approximately 1 cc.

Since the volume of the gas phase was almost 3500 cc, the total pressure was but slightly affected by these conditions.

The results were subject to one source of error, the value of which is unknown but the maximum value of which could be calculated. This arose from the fact that the gas in the container A′ was not circulated and hence may have differed somewhat in composition from the gas in the rest of the apparatus. The maximum error would have occurred if only inert gas were present in A′ and would have amounted to 1 mm in the case of carbon dioxide and ether. The observed differences between the partial pressures and the vapour pressures in the cases of carbon dioxide-ether and carbon-dioxide-acetone might have been due in part to this source of error and in part to a solubility effect although the differences are so small that accidental errors may have been the major factor.

Results and Discussion

The partial pressures and vapour pressures determined by us are given in Table I. The values lying along the same horizontal line were obtained with the same liquid sample. The table also includes a few independent vapour pressure measurements.

The vapour pressure obtained for acetone agrees almost exactly with the value given by Sameshima and is slightly lower than our previously determined value for dry acetone. Our new value supports our previous determination since the specific gravity determination indicated that the original acetone sample was probably the drier of the two. Campbell observed that the partial pressure of methyl alcohol in carbon dioxide at 40°C. was 191 mm whereas the vapour pressure is roughly 260 mm, and offered, as a tentative explanation of this and similar discrepancies, the hypothesis that some sort of adsorption took place at the liquid surface. In our experiments the gas phase was circulated over the liquid phase so that there was ample opportunity for such a phenomenon to occur, if indeed, it were possible. Moreover the stoppage of the circulating pump did not give rise to an increase of pressure but to an almost negligible decrease. We must therefore conclude that such large discrepancies, as have been observed, are due to the particular experimental conditions and are not due to any factor effecting the theoretical principles which have been commonly accepted.

TABLE I

The vapour pressures of volatile liquids and the partial pressures of their vapours in the presence of dry air and dry carbon dioxide

Liquid	t°C.	Air		Carbon Dioxide		True Vapour Pressure	Indep. Vapour Pressure Measurements*	
		Air Pressure	Vapour Partial Pressure	CO_2 Pressure	Vapour Partial Pressure		Vapour Pressure	Observer
Methyl Alcohol	25.00					124.3	122.7	Dittmar and Fawsett
	”	268.4	123.6			122.8		
	”	412.0	123.7			123.9		
	”			390.7	124.2			
				198.1	123.7			
	40.00	225.1	259.5			259.9	259.4	Dittmar and Fawsett
	”			295.0	261.1		260.5	Ramsay and Young
Ethyl Alcohol	40.02	300.6	134.5			134.6	134.3	Interpolated from the results of Schmidts
	”			305.2	134.7			
Acetone	30.00	264.2	283.1			282.9	282.7	Sameshima
	”			250.0	281.7		283.7	Beare and McVicar
Ether	20.00	200.1	442.0			441.6	442.4	Ramsay and Young
	”			198.2	439.8			
	”			192.3	440.4			

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* Dittmar and Fawsett: Trans. Roy. Soc. Edin., **33**, II, 509 (1886-7); Ramsay and Young: Phil. Trans., **177**, 1, 123 (1886); **178A**, 57 (1887); Schmidt: Z. physik. Chem., **8**, 628 (1891); Sameshima: J. Am. Chem. Soc., **40**, 1482 (1918); Beare and McVicar: J. Phys. Chem., **34**, 1310 (1930).

Summary

(1). The partial pressures of methyl alcohol, ethyl alcohol, acetone and ether were determined in the presence of dry air and dry carbon dioxide. The determinations in the presence of air were carried out with liquid samples which were subsequently used for the determination of the vapour pressure without removal from the all-glass apparatus.

(2). The differences between the partial pressures and the vapour pressures were usually less than one millimeter. The large discrepancies which had been previously reported, were not observed.

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THE RELATION BETWEEN OBSCURING POWER AND PARTICLE NUMBER AND SIZE OF SCREENING SMOKES

Object

The object of the work described in this paper was to check the theoretical assumption that the screening power of smokes and clouds is simply related to their particle number and size and to determine the numerical value of that relationship. In addition to this, data were desired on the absorption of moisture by hygroscopic smoke particles, the composition of smoke particles, the efficiency of dispersion, and the stability of smoke clouds.

Historical

No previous experimental work is known which relates the obscuring power of smokes or clouds with the particle number and size. The fact that such a relationship exists was quite accurately forecast by H. W. Walker[1] on purely theoretical grounds. A closely allied line of work consists in a correlation of particle size (concentration remaining constant) with intensity of the Tyndall beam in aqueous colloidal suspensions. Relevant data include work by Mecklenburg[2] who worked with graduated suspensions of colloidal sulfur particles, and Tolman[3] and his collaborators, who worked with graduated suspensions of silica particles. Tolman extended his work in a qualitative way to rosin smokes. Mecklenburg's work covered the range from 0.05×10^{-5} to 8.4×10^{-5} cm. diameter. Tolman's quantitative work covered the range from 10×10^{-5} to 206×10^{-5} cm. diameter. His qualitative work with smokes covered the range from 0.5×10^{-5} to 10×10^{-5} cm.

Although there is some discrepancy in the results of the two investigators named above the following points seem well established:

1. For particle diameters below that of the wave-lengths of light, the intensity of the Tyndall beam increases with an increase in the size of the particles, concentration remaining constant.
2. For particle diameters above that of the wave-lengths of light, the intensity of the Tyndall beam decreases with increase in the size of the particles, concentration remaining constant.
3. For particle diameters of the order of magnitude of the wave lengths of light, the evidence is conflicting but it is evident that this is the transition range. The range of wave-lengths of visible light is from about 4×10^{-5} to about 7.5×10^{-5} cm. The average wave-length of white light is about 5.7×10^{-5} cm.

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[1] Walker: Ind. Eng. Chem., **17**, 1061 (1925).

[2] Mecklenburg, Kolloid-Z., **16**, 97 (1925).

[3] Tolman et al.: J. Am. Chem. Soc., **41**, 300, 575 (1919).

Theoretical

It is known that the absorption of light by true solutions depends upon the thickness of the layer traversed and on the molecular concentration in that layer.[1] Svedberg has shown that the mechanism of light absorption may be the same for colloidal solutions composed of observable particles and for molecular solutions.[2] Ostwald has also shown that, in many cases, absorption by a colloidal solution of a very high grade of dispersion approximates absorption by the corresponding molecular solutions.[3]

It is by no means certain, however, that the mechanism of screening by smokes is as simple as the absorption of light by the smoke particles. Among other factors which might conceivably affect obscurance are reflection and refraction of light, composition of the smoke particles, relative position of observer, smoke and target, and intensity and location of the light source.

Nature of the Problem.—The relation between the obscuring power of smokes and the number and size of the smoke particles may be expressed specifically as the ratio between the sum of the projections upon the surface of the target for all the smoke particles between the eye and the target, and the area of the target when it is just obscured in the smoke cloud. This ratio is referred to in this paper as the "screening ratio" and designated by the letter R. In order to establish a relation of this kind it is necessary either to use smokes in which the particles are all of the same size, or to know the proportionate number of particles of each size present. We may assume, however, from a study of the Brownian Movement, and from other considerations, that the greater number of particles in any stable smoke are essentially of the same size.

Most of the efficient smokes are hygroscopic in character, absorb large quantities of water, and produce spherical liquid particles. Therefore, the area of a great circle through the sphere may be regarded as the projection of the particle upon the vertical target.

From the above it is obvious that the essential data necessary to establish the desired relationship are the number of smoke particles per unit volume, the average size of these particles and the screening power of the smoke. The number of particles may be found with sufficient accuracy by means of the ultramicroscope. Knowing the number of particles per cubic centimeter, the average diameter of the particles may be calculated from the weight and density of the smoke. This involves sampling and analyzing the smoke from a known volume of air. The obscuring power of the smoke may be determined by noting the distance at which a target just disappears from view while under constant illumination.

Experimental

Experimental work was carried out under accurately controlled conditions in a smoke chamber of approximately 63,000 cubic feet capacity and 1,000 square feet cross-sectional area. It was fairly air-tight and provided with ventilating ducts and a large circulatory fan for keeping the smoke uniform in concentration throughout. The chamber was also provided with facilities for humidifying and drying the air to any degree of humidity desired.

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[1] Taylor: "Treatise on Physical Chemistry," 2, 1207.

[2] Svedberg: "Colloid Chemistry," 194 (1928).

[3] Ostwald: Kolloidchem. Beihefte, 2, 409 (1910-11).

Obscuring Power. Observations of the obscuring power of the smoke were made through a small window in one end of the chamber upon a circular, black, 10-inch target mounted 4 feet above the floor. The target was mounted upon an iron rod set in a supporting frame directly in line with the observation window. The target was moved back and forth by means of the iron rod which was graduated in feet. The target was illuminated by two rows of overhead lamps, each row containing fourteen 60-watt lamps, set over the target and about 16 feet above it. Visibility readings were taken one or two minutes after the start of each run and at intervals thereafter. These values were plotted in a visibility-time curve and the values used in the work were read from these curves.

Particle Number. Particle number was determined by means of an ultramicroscope arranged upon a shelf on the outer wall of the smoke chamber near the observation window. The smoke was drawn into the cell through a 1/4-inch glass tube about 12 inches long which projected into the smoke chamber. The source of light for the ultramicroscope was a direct current carbon arc. An optical system projected a fine pencil of light into the observation cell. An absorption cell of cupric chloride solution was used to eliminate the short rays and prevent convection currents in the cell. In order to reduce the personal error of the observer to a minimum the illuminating beam was cut off for brief regular intervals by means of a rotating sectored disk placed in its path. The depth of focus of the microscope was 0.0444 mm. A diaphragm with two small circular apertures was inserted in the eyepiece. The apparent diameters of the apertures were 0.150 and 0.120 mm., determined by focusing on a millimeter scale. The average of fifty successive counts was taken. From the particle count, the depth of focus and the diameter of the aperture used, the number of smoke particles per cubic centimeter was calculated.

Smoke Samples. Samples of the smokes were taken by drawing 20 liters of air-smoke mixture through specially prepared filter tubes with filter beds of ground, fritted glass and thin asbestos mats. The filter tubes were weighed immediately before and immediately after the collection of samples. Great care was exercised to keep the tubes at equilibrium with the moisture of the room. The composition of the smoke was determined by analysis for the chief constituent. From the composition of the smoke particles their density was determined either by reference to standard tables or by special experimental work.

Materials. The smokes used were those which, upon dispersion in air of ordinary humidity, will become liquid droplets. For the liquid smoke materials, dispersion was accomplished by means of an efficient spray. White phosphorus was burned in an open pan and zinc chloride was dispersed by means of a smoke candle containing the so-called H.C. smoke mixture. Ammonium chloride was dispersed by atomizing liquid ammonia and 32%

aqueous hydrochloric acid. The several smoke materials used are shown below:

- Titanium tetrachloride
- Oleum
- Chlorsulfonic acid
- White phosphorus
- Zinc chloride
- Ammonium chloride

In the case of most of the smokes generated, upon dispersion in a humid atmosphere, hydration, hydrolysis or deliquescence occurs. The resulting smoke particles are aqueous solutions of the resulting products. In the case of chlorsulfonic acid, analysis of the smoke revealed only traces of hydrochloric acid and it was assumed that this product of hydrolysis escaped from the liquid droplets. The case of titanium tetrachloride presented a difficult problem on account of the complicated chemical reactions which occur between $TiCl_4$ and water. As a consequence of the uncertainty as to the composition of this smoke some special work was done on the densities of titanium compounds. Mixtures were made up containing varying percentages of titanium tetrachloride and water and these mixtures were analyzed for titanium and their densities determined. It was found that when the densities of the titanic acid solutions were plotted against their titanium content, a straight line was obtained. The values for the density of the particles of titanium tetrachloride smoke were taken from this graph.

The several smoke materials used are tabulated below along with the bases to which the analyses of the smoke samples were calculated.

Smoke Material	Analyzed for
Zinc chloride	$ZnCl_2$
White phosphorus	P_2O_5
Titanium tetrachloride	TiO_2
Ammonium chloride	NH_4Cl
Oleum	SO_3
Chlorsulfonic acid	SO_3

Method of Calculation. The radius of a particle is determined from the equation:

$$r = \sqrt[3]{\frac{3M}{4\pi dN}}$$

where

M = total mass of the particles in 1 cc. (g).
d = density of the particles (g./cc.)
N = number of particles (no./cc.)
r = radius of particle (cm.)

The screening ratio, R, is determined from the equation:

$$R = \frac{\pi D^2 NV}{4}$$

where

D = diameter of a smoke particle (cm.)
V = distance between the eye and the target when the target is just obscured (cm.)
R = the screening ratio.

TABLE I

Zinc Chloride

R.H.	Time after dispersion min.	Number particles $N \times 10^{-6}$	Wt. sample from 20 l. mg.	$ZnCl_2$ by anal. mg.	Diam. of part. $D \times 10^4$ cm.	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	3.50	9.3	3.25	0.547	1.55	153	1.25
	16	1.94	9.5	2.70	0.691	1.42	198	1.44
	26	1.07	8.6	2.17	0.826	1.36	268	1.54
90	6	3.49	14.4	3.94	0.657	1.39	143	1.69
	16	2.24	11.4	2.80	0.711	1.35	192	1.71
	26	1.56	9.3	1.54	0.776	1.22	259	1.91
60	6	3.57	6.5	2.52	0.474	1.63	195	1.23
	16	2.12	4.2	2.25	0.472	1.80	293	1.09
	26	1.15	3.6	2.04	0.550	1.80	390	1.06
60	6	4.16	12.0	3.76	0.570	1.49	198	2.10
	16	2.24	5.1	1.55	0.529	1.47	290	1.43
	26	1.43	4.2	1.36	0.572	1.50	403	1.48
							Ave.	1.49

TABLE II

White Phosphorus

R.H.	Time after dispersion min.	Number particles $N \times 10^{-6}$	Wt. sample from 20 l. mg.	P_2O_5 by anal. mg.	Diam. of part. $D \times 10^4$ cm.	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	2.68	25.7	3.69	0.938	1.11	198	3.66
	16	1.84	19.7	2.48	0.976	1.10	247	3.40
	26	1.10	15.2	1.93	1.063	1.10	326	3.18
90	6	3.65	35.1	3.71	0.947	1.08	204	5.25
	16	1.89	25.5	2.62	1.061	1.08	250	4.18
	26	0.94	19.2	2.03	1.218	1.08	317	3.47
							Av.	3.86
60	6	2.78	4.9	3.23	0.467	1.65	250	1.19
	16	1.35	3.3	1.96	0.526	1.60	311	0.91
	26	1.10	3.4	1.91	0.573	1.57	412	1.17
60	6	2.78	5.9	3.46	0.502	1.60	275	1.51
	16	1.25	4.0	2.77	0.570	1.65	384	1.22
	26	1.10	3.8	1.73	0.610	1.45	494	1.59
60	6	1.86	8.5	3.46	0.678	1.40	262	1.76
	16	1.89	4.2	1.91	0.527	1.45	357	1.47
	26	1.25	4.2	1.85	0.606	1.44	519	1.87
							Av.	1.41

Experimental Data. The experimental data and the screening ratios calculated therefrom are shown in Tables I to VI. For each smoke tested, runs were made at 60 and 90 per cents relative humidity in order to test the effect of humidity upon particle number and size. The actual humidities were within about one per cent of the humidities desired. Temperatures were recorded but as they had no discernible effect upon the results of the tests they are omitted from the tables. Samples of the smoke were taken and observations were made at 6, 16, and 26 minutes after dispersion of the smokes.

TABLE III

Titanium Tetrachloride

R.H.	Time after dispersion min.	Number particles $N \times 10^{-6}$	Wt. sample from 20 l. mg.	TiO_2 by anal. mg.	Diam. of part. $D \times 10^4$ cm.	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	4.82	16.8	3.86	0.614	1.44	101	1.44
	16	1.86	7.6	3.04	0.599	1.82	171	0.90
	26	1.40	10.8	2.54	0.796	1.46	250	1.74
90	6	6.17	10.8	1.51	0.513	1.24	134	1.71
	16	2.96	3.8	1.21	0.421	1.64	247	1.02
	26	1.86	2.2	0.95	0.391	1.89	320	0.71
90	6	5.73	16.7	3.22	0.589	1.36	82	1.28
	16	2.86	13.0	3.18	0.664	1.48	146	1.45
	26	2.30	6.4	2.54	0.527	1.82	207	1.04
90	6	3.62	9.6	2.02	0.566	1.40	104	0.95
	16	1.38	4.4	1.68	0.555	1.78	204	0.68
	26	1.02	3.4	1.30	0.563	1.78	320	0.81
60	6	5.85	6.5	4.08	0.358	2.32	186	1.09
	16	2.37	7.3	3.22	0.536	1.91	326	1.74
	26	1.45	3.6	2.42	0.461	2.42	497	1.20
60	6	8.96	10.3	5.00	0.379	2.01	162	1.64
	16	3.60	5.4	3.54	0.391	2.39	302	1.31
	26	1.22	3.5	2.64	0.472	2.61	451	0.96
60	6	5.42	9.9	3.58	0.465	1.74	162	1.49
	16	1.71	6.1	2.78	0.559	1.95	287	1.20
	26	0.87	4.9	1.85	0.672	1.77	448	1.38
60	6	6.21	7.3	3.46	0.384	1.99	162	1.16
	16	3.37	7.9	2.70	0.510	1.69	290	1.99
	26	1.53	3.5	1.95	0.465	2.17	464	1.20
								Av. 1.25

TABLE IV

Ammonium Chloride

R.H.	Time after dispersion min.	Number particles $N \times 10^{-6}$	Wt. sample from 20 l. mg.	NH_4Cl by anal. mg.	Diam. of part. $D \times 10^4$ cm.	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	5.26	8.1	1.09	0.521	1.04	143	1.60
	16	2.65	—	—	—	—	165	—
	26	1.53	4.4	0.14	0.648	1.01	207	1.04
90	6	4.02	4.2	1.22	0.452	1.08	195	1.26
	16	3.62	—	—	—	—	210	—
	26	2.07	—	—	—	—	241	—
90	6	5.54	10.0	0.95	0.551	1.03	143	1.89
	16	3.04	6.8	0.68	0.592	1.03	156	1.30
	26	2.75	4.8	0.41	0.545	1.03	195	1.25
90	6	4.94	7.3	1.22	0.512	1.05	143	1.46
	16	1.91	2.5	1.09	0.481	1.12	149	0.52
	26	1.35	3.5	0.95	0.612	1.08	189	0.75
90	6	4.66	5.6	0.95	0.478	1.05	180	1.51
	16	2.24	4.9	0.95	0.582	1.06	201	1.20
	26	1.28	2.3	0.41	0.547	1.05	275	0.82
90	6	3.07	1.9	0.68	0.377	1.10	207	0.71
	16	2.19	2.6	0.68	0.472	1.08	217	0.83
	26	1.20	10.4	0.41	0.936	1.01	247	2.04
90	6	2.67	2.5	0.82	0.434	1.09	146	0.58
	16	1.61	3.8	1.22	0.593	1.08	156	0.69
	26	1.30	1.9	0.68	0.502	1.10	192	0.49
75	6	4.34	2.4	1.36	0.356	1.17	650	2.80
	16	1.66	—	0.82	—	—	695	—
	26	0.71	—	0.68	—	—	781	—
75	6	2.91	—	1.22	—	—	592	—
	16	1.10	1.2	0.95	0.436	1.26	708	1.16
	26	1.17	1.9	0.54	0.524	1.08	839	2.11
60	6	3.27	3.0	2.04	0.417	1.21	503	2.24
	16	1.63	1.3	0.82	0.400	1.19	604	1.24
	26	1.15	—	0.54	—	—	750	—
60	6	3.19	—	1.36	—	—	576	—
	16	1.94	2.0	0.68	0.449	1.09	601	1.84
	26	1.17	0.7	0.41	—	—	—	—
60	6	4.34	2.2	1.63	0.340	1.23	461	1.81
	16	2.02	1.0	1.22	0.342	1.18	552	1.03
	26	1.30	0.6	0.68	0.334	1.18	677	0.77
60	6	3.66	3.4	2.18	0.420	1.20	351	1.78
	16	1.96	1.3	2.04	0.377	1.18	439	0.96
	26	0.89	1.9	0.95	0.653	1.14	576	1.28
							Av.	1.30

TABLE V

Oleum

R.H.	Time after dispersion min.	Number particles $N \times 10^{-6}$	Wt. sample from 20 l. mg.	SO_3 by anal. mg.	Diam. of part. $D \times 10^4$ cm.	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	3.60	5.9	2.0	0.500	1.25	320	2.26
	16	2.70	0.8	0.5	0.265	1.52	326	0.49
	26	1.17	0.9	0.25	0.395	1.19	357	0.51
90	6	8.20	21.4	5.4	0.596	1.18	92	2.08
	16	3.19	15.7	4.2	0.734	1.19	122	1.65
	26	2.07	12.7	3.4	0.790	1.19	165	1.67
90	6	4.18	10.8	3.6	0.582	1.25	104	1.16
	16	2.07	5.6	1.5	0.599	1.20	131	0.77
	26	1.07	7.0	2.2	0.798	1.23	174	0.93
90	6	5.02	11.1	3.9	0.542	1.33	85	0.98
	16	2.27	9.4	2.9	0.687	1.22	116	0.98
	26	1.68	7.0	2.2	0.686	1.23	168	1.04
60	6	6.29	12.9	4.4	0.539	1.25	131	1.88
	16	3.65	5.1	2.8	0.452	1.44	174	1.02
	26	1.45	4.6	2.4	0.599	1.41	238	0.97
60	6	3.27	—	—	—	—	143	—
	16	1.71	7.3	3.7	0.663	1.40	189	1.12
	26	1.40	6.5	2.6	0.699	1.30	247	1.33
60	6	3.90	12.5	6.0	0.607	1.37	119	1.34
	16	1.86	6.7	1.5	0.667	1.16	153	0.99
	26	0.99	5.6	2.6	0.735	1.36	210	0.88
								Av. 1.20

TABLE VI

Chlorsulfonic Acid

R.H.	Time after dispersion min.	Number particles $N \times 10^{-6}$	Wt. sample from 20 l. mg.	SO_3 by anal. mg.	Diam of. part $D \times 10^4$	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	—	—	—	—		122	—
	16	1.63	2.1	0.3	0.482	1.10	146	0.43
	26	2.12	3.1	0.1	0.516	1.02	198	0.88
90	6	5.22	6.0	1.1	0.460	1.13	131	1.13
	16	2.70	3.5	—	0.486	1.08	165	0.83
	26	2.83	—	—	—	—	232	—
90	6	5.10	4.6	—	0.430	1.08	131	0.97
	16	2.17	3.0	—	0.496	1.08	156	0.65
	26	1.84	2.8	—	0.512	1.08	201	0.76
60	6	5.26	6.8	1.5	0.474	1.16	232	2.15
	16	2.75	1.3	1.4	0.329	1.27	275	0.64
	26	1.81	2.9	0.6	0.511	1.15	348	1.29
60	6	6.81	4.9	2.1	0.372	1.33	214	1.58
	16	2.17	1.7	1.2	0.359	1.62	241	0.53
	26	1.73	2.8	0.7	0.508	1.18	296	1.04
60	6	5.02	2.7	0.8	0.348	1.22	165	0.79
	16	2.24	0.9	—	0.311	1.27	192	0.33
	26	1.25	0.9	0.3	0.380	1.25	262	0.37
60	6	3.82	4.3	—	0.439	1.27	287	1.66
	16	1.79	3.6	—	0.533	1.27	314	1.25
	26	2.22	—	—	—	—	390	—
							Av.	0.96

Discussion of Data

Screening Ratio. Not including phosphorus smoke at 90% relative humidity the average of the screening ratios is 1.27. If results be omitted which are manifestly out of line, due mainly to very small smoke samples, the average ratio would be somewhat higher than this, in the neighborhood of 1.35. For spheres with uniform packing, the theoretical ratio for complete blocking out of the background is 1.57.

Again excepting phosphorus smoke at 90% relative humidity it will be noted that the diameters of the smoke particles lie substantially between the limits 0.40×10^{-4} cm. and 0.75×10^{-4} cm. which define the range of the wave lengths of visible light. The average diameter of the white phosphorus smoke particles at 90% relative humidity is 1.03×10^{-4} cm. while the average screening ratio is 3.86. The obscuring value of white phosphorus at high humidities is little better than it is at low humidities in spite of the large amount of water absorbed by the particles and their consequently large size.

These data point to the conclusion that for smoke particles whose diameters are within the range of the wave lengths of visible light screening is accomplished by a simple blocking of the light rays. For particles of this size the composition is not a factor. For particles whose diameters are larger than the wave lengths of visible light, screening is accomplished by a different mechanism and the refractive index or other physical properties of the smoke particles may be a factor.

These and other conclusions in this report apply only to white smokes having liquid particles. Some work was also done on a black carbon smoke having solid particles but on account of the irregularity in size and outline the projections of the particles could not be calculated.

It should also be mentioned that the screening ratio named above has been proved to apply only to the experimental conditions which obtain in the smoke chamber used. There is some evidence that smokes are more efficient in screening out of doors than in the smoke chamber. If this is the case, it is probably due to such factors as the relative position of observer, smoke, and target, to the intensity and reflection of light, variation of particle size, and other such causes.

Effect of Humidity. The obscuring power of all the smokes was greater at 90% than at 60% relative humidity, and, in some instances, this was very marked. This was due to the larger size of the particles at the higher humidity caused by the adsorption of moisture. If the absorption of moisture increases the diameter of the particle beyond the wave lengths of light, as in the case of white phosphorus smoke, the increase in screening power is not proportional to the increase in particle size. In the case of ammonium chloride smoke the increase in screening power at 90% relative humidity was very large. By a consideration of the data of Owens[1] with the aid of the vapor pressure of saturated ammonium chloride solutions[2] we were able to show that at 60% relative humidity the ammonium chloride particles were composed of fine crystals, at 90% they were liquid while for the two runs at 75% the particles were just on the border line between liquid and solid. These data check very well with the observed screening power.

The data in the tables give us a means of estimating roughly the amount of water absorbed by the smokes studied. Such an estimate, based on a careful analysis of the data, is shown below. Equilibrium with the moisture in the air is, in all cases but one, reached before 6 minutes and the values shown in the table represent an average of all observations.

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[1] J. S. Owens: Proc. Roy. Soc., **110A**, 738 (1926).

[2] Edgar and Swan: J. Am. Chem. Soc., **44**, 570 (1922).

TABLE VII

Parts of Water absorbed by Smokes

Smoke material	At 90% R.H.	At 60% R.H.
$ZnCl_2$	3	2
P_2O_5	7.5	1
TiO_2	1.5[1]	1
NH_4Cl	5	0.5
SO_3 (from oleum)	2.5	1
SO_3 (from chlorsulfonic acid)	5	2

It is interesting to compare the concentrations represented by the proportions of substance and water shown in the above table with the concentrations of solutions in bulk at equilibrium with air under the conditions of humidity and temperature which obtained in our experiments. In addition to ammonium chloride, which is discussed above, the smokes from phosphorus, oleum, and chlorsulfonic acid lend themselves to such a comparison because for these smokes the composition of the smoke particles is known with a fair degree of accuracy. From the analytical data it is assumed that the smoke from chlorsulfonic acid is composed essentially of sulfuric acid. For sulfuric acid sufficient data exist in the literature for complete vapor pressure curves at any concentration and temperature. For phosphoric acid the data are not so complete. By the aid of the Clausius-Clapeyron equation, however, vapor pressure curves were drawn from the data available for phosphoric acid. A comparison of the theoretical concentrations at equilibrium with the air at the temperatures and relative humidities obtaining in the experiments, with the concentrations represented by the analytical data in tables, is shown below. The comparison is expressed in terms of the ratio of water to SO_3 and P_2O_5, respectively.

TABLE VIII

Comparison between Theoretical and Observed Parts of Water absorbed by Smokes

Smoke	Relative humidity	Ratio H_2O/SO_3 or P_2O_5	
		Theoretical	Experimental
Oleum	90	7	2.5
Oleum	60	2	1
Chlorsulfonic acid	90	8	5
Chlorsulfonic acid	60	2	2
White phosphorus	90	6	7.5
White phosphorus	60	1.4	1.0

The comparison in the above table is as good as could be expected considering the roughly approximate nature of the ratios shown in Table VII. There is a tendency for the experimental values to be lower than the theoretical ones. This is probably due primarily to the well known fact that the vapor pressure of small particles is appreciably higher than for the same liquid in bulk, tending to concentrate fine droplets of solutions.

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[1] In this case the absorbed water at 6 minutes is distinctly more than at 16 and 26 minutes, and amounts to about 3 parts.

Efficiency of Dispersion and Stability of the Smoke Cloud. The efficiency of the method of dispersion employed may be judged by the amount of smoke material in the air at the end of 6 minutes while the stability of the cloud may be judged by the relative amounts still remaining in the air after 16 and 26 minutes. From the analyses of the samples of smoke collected from 20 liters of air the averages of the amounts of the several original materials found present at the end of 6, 16, and 26 minutes have been calculated and expressed in terms of percentages of the weight of substance originally dispersed. Both humidities have been averaged in together as the recovery was about the same for both. These figures are shown in the following table together with the percentage decrease from 6 to 26 minutes. These last figures represent the stability of the cloud.

TABLE IX

Efficiency of Dispersion and Stability

Substance	Amount found[1] in % of original substance after			Percentage decrease
	6 min.	16 min.	26 min.	6-26 min.
H. C. candle	53.0	37.3	28.3	48
W.P.	68.3	45.4	36.8	46
F.M.	74.0	59.0	44.8	40
Oleum	53.6	28.0	26.0	51
Chlorsulfonic acid	15.2	12.4	4.6	63
NH_4Cl	20.4	16.1	9.0	56

When the percent of smoke still in the air from Table IX are plotted on the logarithmic scale against the time in minutes, on semi-log paper the points define straight lines which are practically parallel. The intersection of these lines on the ordinate representing zero time represents the actual efficiency of dispersion expressed in terms of per cent of the original substance taken. The efficiencies determined in this manner are shown in Table X.

TABLE X

Actual Efficiency of Dispersion of Smokes at Zero Time

Substance	Efficiency as % of original substance
H.C.	65
W.P.	80
F.M.	87
Oleum	66
Chlorsulfonic acid	20
NH_4Cl	32

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[1] Calculated back to the original material dispersed.

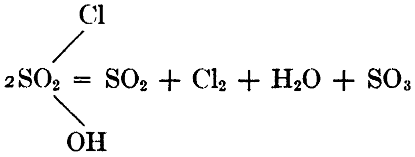
The low efficiencies of dispersion for chlorsulfonic acid and ammonium chloride smokes are probably due to insufficient heat to bring about decomposition in the case of the former and incomplete reaction between NH_3 and HCl in the case of the latter. The stability is about the same for the six smokes studied, chlorsulfonic acid being the most unstable. This again is probably due to inefficiency of the method of dispersion. The average decrease between 6 and 26 minutes is 50%.

On the whole, Table X indicates a much lower efficiency of dispersal than is ordinarily assumed. It should be emphasized that these efficiencies are calculated in a manner which eliminates the effect of precipitation and leakage in the smoke chamber. There is, therefore, no reason to believe that dispersal out of doors, by the same methods, is more efficient than the figures shown in this table.

The stability of a highly non-volatile cloud out of doors is certainly greater than in the smoke chamber. In the main two opposing factors are operative. One of these is the precipitation of smoke particles in the chamber, due to forced ventilation. This occurs particularly around the fan blades and at the bends in the ventilating ducts. (There is also a small but unknown amount of leakage.) The other factor is the increased tendency to evaporation out of doors where the cloud is being continually diluted with fresh air.

Composition of the Smoke Particles. We are justified in the assumption that smokes from the H.C. smoke candle, white phosphorus; oleum, and ammonium chloride consist, respectively, of droplets of $ZnCl_2$, P_2O_5, SO_3 and NH_4Cl with water since there is no likelihood of any further reaction of these constituents.

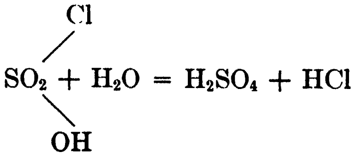
In the case of chlorsulfonic acid it is known that heat is necessary for an efficient dispersal. It is stated in Thorpe's "Dictionary of Applied Chemistry," **5**, 301, that chlorsulfonic acid is decomposed by heat according to the following equation:



$$2SO_2\begin{smallmatrix}\diagup Cl\\ \diagdown OH\end{smallmatrix} = SO_2 + Cl_2 + H_2O + SO_3$$

The reaction is complete when the vapors are heated to 200°C.

Chlorsulfonic acid also reacts with water according to the following equation:



$$SO_2\begin{smallmatrix}\diagup Cl\\ \diagdown OH\end{smallmatrix} + H_2O = H_2SO_4 + HCl$$

If the first reaction takes place before the chlorsulfonic acid is exposed to the moisture of the air, and if the temperature is sufficiently high to bring about complete decomposition, the part of the products represented by SO_2 + Cl_2, being gaseous, is lost for the formation of smoke while the part represented by H_2O + SO_3 is completely utilized. This latter part represents only 42% of the original molecule. If chlorsulfonic acid is atomized in the cold we might expect a more complete utilization of the original molecule, but the fact that this is not true indicates that the cold chlorsulfonic acid may fall out of suspension before it has a chance to react with the moisture of the air. In the work described in this report chlorsulfonic acid was atomized by means of a rapid current of CO_2. Both the container holding the chlorsulfonic acid and the CO_2 line were heated by steam, the temperature varying from 115 to 135°C. The reaction with heat was, therefore, incomplete. The evidence, therefore, indicates that at least a portion of the original chlorsulfonic acid, not decomposed by heat, fell out of suspension soon after atomization. This theory is strengthened by the fact that analyses of the samples collected from this smoke showed but traces of HCl and also by the very low recovery of this smoke after 6 minutes. This theory indicates that the most efficient method to disperse chlorsulfonic acid is to heat the vapors to a temperature somewhat over 200°C before discharging them into the air, but then only 42% of the original material could be utilized. A somewhat higher efficiency than this might be obtained by a very efficient atomizer, using steam as the atomizing agent. Disregarding the HCl an efficiency of about 70% is theoretically possible by this method. Some work has been done on the use of steam and it has been found that superheated steam gives a good smoke.

The composition of the smoke by either method would be droplets of sulfuric acid, the HCl being driven out by the heat of the reaction.

The case of the composition of the smoke from titanium tetrachloride is more obscure and little seems to be known about the reaction of this substance with water. Consequently, some study was made of the data for this smoke and some additional experimental work was done in an effort to determine its composition. Unfortunately, the samples of smoke taken during the counting experiments were not sufficiently large to analyze for both TiO_2 and HCl. Therefore, additional samples were collected and analyzed for HCl. The data from these analyses admit of only a rather rough estimate of the amount of HCl in these smokes. The percentage of HCl is somewhat more at 90% than at 60% relative humidity. The percentages of HCl present in the smoke at different time intervals and humidities is approximately as follows:

	60% R.H.	90% R.H.
At 6 min.	13	19
At 16 min.	13	17
At 26 min.	8	10

Calculations of the composition of the smoke represented by the data in Table III were made on the basis of the above average contents of HCl. Though the individual variations in composition are quite large, it is probable that average figures are fairly representative of these smokes. The results expressed in percentages of TiO_2, H_2O, and HCl are shown below.

TABLE XI

Composition of Titanium Tetrachloride Smoke in Percentages

Time	60% R.H.			90% R.H.		
	TiO_2	H_2O	HCl	TiO_2	H_2O	HC
6 minutes	49	38	13	19	62	19
16 minutes	47	40	13	28	55	17
26 minutes	59	33	8	36	54	10
Average	52	37	11			

The composition of the smoke at 60% relative humidity appears to be fairly constant from 6 to 26 minutes, and is represented by the following:

$$2\ TiO_2 + 6\ H_2O + HCl$$

or the composition may be written

$$Ti(OH)_4 + H_2O + 1/2\ HCl$$

Under ordinary conditions of moisture, it appears that the compound originally formed, $TiCl_4.5H_2O$, begins at once to hydrolyze, splitting off HCl which escapes from the particles quite readily since most of it is gone in 6 minutes.

At 90% relative humidity the relative proportions of H_2O and HCl change rather rapidly after the first 6 minutes. The compositions at 6, 16, and 26 minutes are represented approximately by the following:

At 6 minutes.................. $Ti(OH)_4 + 12\ H_2O + 2\ HCl$
At 16 minutes................. $Ti(OH)_4 + 7\ H_2O + 1.5\ HCl$
At 26 minutes................. $Ti(OH)_4 + 4\ H_2O + 0.5\ HCl$

The change in composition is due to the loss of both H_2O and HCl. Hydrolysis of the $TiCl_4.5H_2O$, which was probably first formed, is complete before 6 minutes when the composiion of the smoke is a solution of $Ti(OH)_4$ with some HCl dissolved in it.

Limits of Accuracy. The effect of several sources of error in these experiments are briefly discussed below.

The depth of focus of the microscope was utilized in determining the volume of the field containing the particles to be counted. The normal eye is capable of accommodation within limits; consequently, the depth of focus utilized by the observer in viewing the particles may differ from the depth of focus as determined experimentally. It is also not necessarily true that only the particles falling within the depth of focus appear as points of light and not as disks. Particles too small to be detected by the ultramicroscope may have been present, but it is thought that the effect of this error would be negligible. These above mentioned errors would affect all the results to the same degree. Whytlaw-Gray,[1] in a recent article discusses the errors due to the scattering of light within the cell by the smoke particles.

It was thought possible that the filters might not collect the smallest particles present. A check was made by placing two filters in series, but the second filter showed no increase in weight. If any errors were introduced in this manner they were quite small.

The density of the smokes read from tables and determined experimentally probably does not exactly represent the density of the particles in the cloud, and the errors may be considerable in some cases.

Most of the smokes examined are hygroscopic and hence very sensitive to conditions of humidity and temperature. It was, therefore, important to weigh the samples of smoke immediately after collecting them to avoid errors due to a change in weight due to loss or gain of moisture. The temperature of the observation room was kept as near as possible to that of the smoke chamber but the humidity could not be controlled. When the humidity of the observation room was markedly different from that of the smoke chamber and the smoke being tested was a very hygroscopic one, like phosphorus, the error due to this cause was likely to be considerable.

It is thought that errors in the visibility readings of the target were probably of less importance than many of the other errors. The illumination and the point of observation from the cloud were constant for all smokes, and any divergence in this respect from the true obscuring power would be constant. The chief error would lie in the personal factor of the observer's eyesight.

Conclusions

1. For smokes consisting of spherical particles of diameters within the range of the wave lengths of visible light the average of the screening ratio (ratio of the total cross-sectional areas of the smoke particles to the area of the target) is 1.27. It is indicated that the correct ratio is somewhat higher than this, probably about 1.35. This ratio holds true for the conditions under which the smoke measurements were made in the smoke chamber.

2. For particles of diameters within the range of the wave lengths of visible light (0.40 to 0.75×10^{-4} cm.) the screening power is independent of the composition of the smoke particles and dependent solely upon the number and size of the smoke particles between the eye and the target.

3. Phosphorus smoke at 90% relative humidity consists of particles considerably larger than the wave-lengths of visible light. The average value of the screening ratio for this smoke is 3.86. It is indicated that particles of this size screen by a different law from that applying to particles of diameters equal to the wave-lengths of light. Some light may go through the large phosphoric acid solution particles. It is possible that for particles larger than the wave lengths of light the physical properties of the substance of which the particles are composed, in particular the refractive index, may be a factor.

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[1] Proc. Roy. Soc., **116A**, 540 (1927).

4. For smokes having particle diameters within the range of the wave-lengths of visible light, there is no evidence of any regular change in the value of the screening ratio with the change in size over the comparatively small range within which the particles for these smokes vary.

5. The results suggest that under the conditions obtaining in the smoke chamber, smokes consisting of particles whose diameters are within the range of the wave-lengths of visible light obscure a non-luminous target when the number of particles between the eye and the target are sufficient, when projected, to form a uniform layer of approximately one particle in thickness. The actual average ratio as stated above was 1.27, but it is indicated that the correct ratio is somewhat higher than this. For spheres with uniform packing the theoretical ratio for complete blocking out of the background is 1.57.

6. The obscuring power of efficient smoke-producing materials is to a large extent due to atmospheric moisture which is absorbed from the air by hygroscopic smoke particles. This is the explanation of the superior obscuring power of smokes at high humidities. It is indicated by the case of phosphorus smoke, however, that there is an upper limit beyond which the absorption of water from the air fails to be reflected proportionally in increased obscuring power of the smoke. This limit is reached when the smoke particles exceed in diameter about 0.75×10^{-4} cm.

7. For all the smokes studied the precipitation in the smoke chamber followed a logarithmic law, according to which the logarithm of the amount remaining in the air at any given time was proportional to the time.

THE ADSORPTION OF CERTAIN VAPORS BY ACTIVATED CHARCOAL. III.

BY J. N. PEARCE AND A. L. TAYLOR[1]

All experimental research on adsorption, hitherto, has been directed, for the most part, to the solution of two closely related fundamental problems. These problems involve, (1) the determination of the nature, the extent and range of the forces which are instrumental in producing concentration changes in the gas phase at the solid-gas interface, and (2) the determination of the physical states and of the chemical relationships existing in the adsorption system.

Whenever adsorption is mentioned we naturally think of the monumental work of Langmuir.[2] He has shown that in many cases, especially on plane metallic surfaces, the adsorbed layer is but one molecule thick, often only partially covering the adsorbing surface, and that the adsorbed molecules are highly oriented with respect to the adsorbent. With him adsorption is distinctly a chemical phenomenon.

The whole problem of adsorption becomes much more complicated when the adsorbent presents a rough uneven surface, like amorphous charcoal. Here we not only have the possibility of an increasing preferential adsorption as we pass from surfaces to edges to points,[3] but also the influence of capillarity.

The complete solution of the adsorption problem will require an accurate knowledge not only of the physical properties of the adsorbent, but also of the adsorbate as well. Among the latter are surface tension, capillarity, compressibility, and the heats of condensation, of wetting and adsorption. In case of the highly porous bodies which possess fine capillaries the geometrical configuration of the adsorbed molecules, their size and structure, the chemical and electrical nature of the molecules and of the substituents in these molecules,—all of these must exert a pronounced influence upon the energy and the magnitude of the adsorption of vapors.

In any heterogeneous system in which one phase is rigid and one mobile there will always be, according to Gibbs,[4] a change in concentration of the mobile phase at the interface, if such a change in concentration will result in a decrease in surface energy. Langmuir[5] has shown that in forming films on liquids the molecules of the paraffin hydrocarbons arrange themselves in such a way that the methyl group (CH_3) forms the surface layer. No matter how long the chain may be the surface energy of the series from hexane to the molten paraffins is practically the same. The surface energies of the alcohols are practically the same as those of the hydrocarbons. Further, a bulky end group, like "I" or "NO", greatly increases the surface tension of the paraffins just as the substitution of an "OH" group, by orientation, increases the surface energy of benzene. He was able to show conclusively that the molecules are highly oriented in these surface films.

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[1] An extract of a thesis presented by A. L. Taylor in partial fulfillment of the requirements for the Ph.D. in Chemistry at the State University of Iowa.

[2] Langmuir: Phys. Rev. (2), **6**, 79 (1915); **8**, 149 (1916); J. Am. Chem. Soc., **38**, 2221 (1916); **40**, 1361 (1918).

[3] Taylor: J. Phys. Chem., **30**, 145 (1926).

[4] Gibbs: "Scientific Papers," **1**, 219 (1906).

[5] Langmuir: Met. Chem. Eng., **15**, 468 (1915).

We have been working for some time upon a systematic study of the relation between adsorption magnitudes and the various physical and chemical properties of the vapor molecules. To this end the vapors studied have been taken up in a definite order, viz., the order in which they occur in an homologous series, or in the order of increase in the number of a substituent atom or group in a given molecule, and, finally, from the standpoint of isomeric modifications, involving straight and branched chain compounds.

Our first contribution[6] deals with the adsorption of water, methyl alcohol, ethyl alcohol, ammonia, and methylamine vapors by activated charcoal; the second[7] presents the results of a study of the adsorption of methane and its chlorine derivatives. In these we have assumed that it is the oxygen, the nitrogen, and the chlorine atom, respectively, that is most strongly attracted by the carbon atoms in the surface lattice of the adsorbent. The chlorine derivatives of the hydrocarbons are particularly interesting in the study of adsorption in that the chlorine atom possesses a large number of valence electrons. The force fields about this atom, and hence its residual valence, should be large. Moreover, the chlorine atom is usually considered to be highly electronegative, and hence the substitution of a chlorine atom for hydrogen must increase the electronegativity of the molecule.

The present work presents the results of the study of the adsorption isotherms of two series of vapors. These series are closely related in adsorptive forces and each offers special opportunities for the study of the structure of surface films and of the forces involved in the formation of these films. The isotherms of methyl chloride,[7] ethyl chloride, n-propyl chloride and n-butyl chloride make available data on four alkyl chlorides of an homologous series in which the lengths of the carbon chain of successive members differ by a constant increment, CH_2. By including the study of the vapors of isopropyl chloride and tertiary butyl chloride we have a second series in which one, two and three of the hydrogen atoms of the methyl radicle are replaced by methyl groups. If we remember that these molecules are oriented with the chlorine atom toward the surface of the charcoal, it is evident that we have a series in which the cross-sectional area of the molecule, in a plane parallel to the surface of the adsorbent, is increased by characteristic increments. We may thus produce a crowding effect on the immediate surface, but at some distance from the surface.

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[6] Pearce and Knudson: Proc. Iowa Acad. Sci., 34, 197 (1927).

[7] Pearce and Johnstone: J. Phys. Chem., 34, 1260 (1930).

Materials and Apparatus

The "acid-washed", "acid-free", steam-activated charcoal used in this work was taken from the same large supply as that used in the previous researches[6],[7]. It was specially prepared for us from coconut shell by the Carbide and Carbon Chemicals Corporation, under the direction of Dr. N. K. Chaney. The loss in weight on outgassing was found to be 2.5 percent; the density of the outgassed charcoal is 1.80[6]. These values were always employed in calculating the actual weight of the charcoal used and in calculating the volume of the dead "space." All samples of charcoal used were outgassed at 525° until the pressure dropped to about $0.5.10^{-4}$ mm. and the charcoal was then allowed to cool to room temperature where the pressure was too small to be measured on a McLeod gage.

The liquid alkyl chlorides used in producing the vapors were of the highest quality obtainable from the Eastman Kodak Co. Each liquid was further purified by careful repeated fractionation. The last three or four fractionations were carried out in an air-free apparatus of such design that the vapor never came in contact with air before it was brought in contact with the charcoal. The boiling points of the purified alkyl chlorides were: ethyl chloride, 12.5° at 755 mm.; n-propyl chloride, 46.5° at 753 mm.; iso-propyl chloride, 34.65° at 748.6 mm.; n-butyl chloride, 77.0°-77.2° at 745 mm; ter-butyl chloride, 50.1° at 740.45 mm.

The apparatus and the experimental procedure was the same as that employed in the work of Pearce and Johnstone.[7] The apparatus was, however, carefully recalibrated. Adsorption equilibrium was assumed when the pressure of the vapor above the charcoal remained constant for at least 30 minutes. In those cases where equilibrium was only slowly attained a much longer time was allowed. Each pressure reading recorded is the mean of at least two or three readings and is corrected to 0°, sea level and 45° latitude. Each isotherm plotted represents at least two different series of measurements on different samples of charcoal. An isotherm was considered as definitely established when the points of successive series were found to lie on the same smooth curve.

To furnish a better basis of comparison the isotherms of the five alkyl chlorides were determined as nearly as possible at the same temperatures. The lowest temperature employed for each vapor was 0°; the highest temperature used depended upon the stability of the vapor in contact with the charcoal. The temperature of each isotherm was frequently checked by raising or lowering the temperature until it corresponded with that of an adjacent isotherm and then by adjusting the volume of vapor in contact with the charcoal so that the point representing equilibrium would fall in the region of high pressures. The equilibrium points thus obtained were in excellent agreement with the isotherm previously determined on a fresh sample of charcoal. Only in one case did we observe any evidence of decomposition. This was for the tertiary butyl chloride at 99.5°.

Natural Isotherms

The adsorption isotherms obtained in this series have the usual characteristic forms. At all temperatures the curves are concave toward the pressure axis throughout the entire pressure range. Attempts to determine the isotherms at temperatures above those for which data were obtained failed because of the occurrence of decomposition as indicated by a progressive increase in pressure over a long period of time. The temperatures at which decomposition of the alkyl chlorides first appeared are: methyl, 236° (rapid); ethyl, 236°; n-propyl, 182°; iso-propyl, 137°; n-butyl, 140°; tertiary butyl, 99.5°. Thus, the stability of the alklyl chlorides in contact with our charcoal decreases with increase in molecular complexity. It is lower for the secondary and tertiary forms than for the corresponding normal compounds.

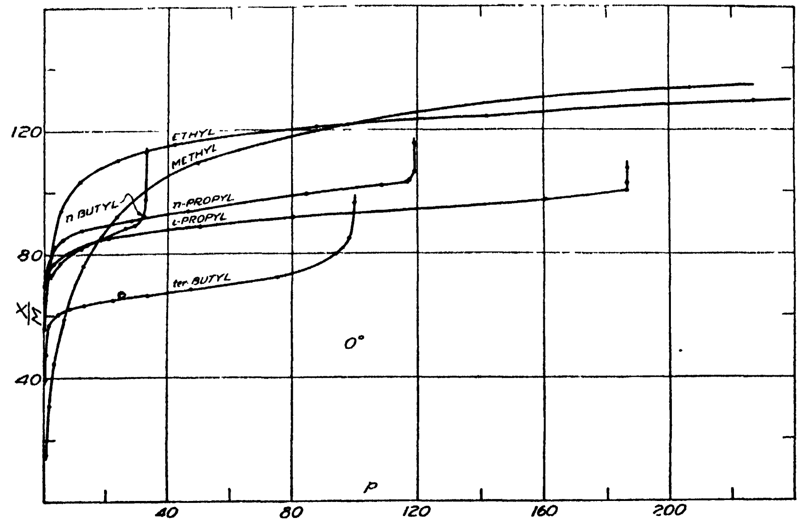

Fig. 1

From the reproducibility of their results Lamb and Coolidge[8] conclude that previous contact with ethyl chloride does not alter the adsorption capacity of activated charcoal for subsequent determinations. Our experience has been exactly the opposite. In no case have we found the activity the same after outgassing at 525°.

The various isotherms for the individual vapors were carefully plotted separately and from these were read the data for the isobars and isosteres. For purposes of illustration we are presenting in Figs. 1-4 the natural isotherms of the alkyl chlorides at 0°, 40°, 77.5° and 99.5°, respectively. The plots of the higher pressures have been purposely omitted to save space. While these temperatures cannot in any way be considered as corresponding adsorption temperatures of the vapors the plots show the characteristic trends of the various isotherms. They show also the influence of temperature upon the relative amounts of the different vapors adsorbed at the various pressures.

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[8] Lamb and Coolidge: J. Am. Chem. Soc., **46**, 1146 (1920).

At 0° the adsorption isotherms break very sharply away from the X/M axis. With rise in temperature the break becomes less pronounced and it should completely disappear in the vicinity of the critical temperature. For a given temperature also the sharpness of the break increases as the boiling point of the liquids increases, but it occurs at lower values of X/M.

The isotherms at 0° (Fig. 1), may be somewhat complicated because of the fact that four of the vapors reach saturation at relatively low pressures.

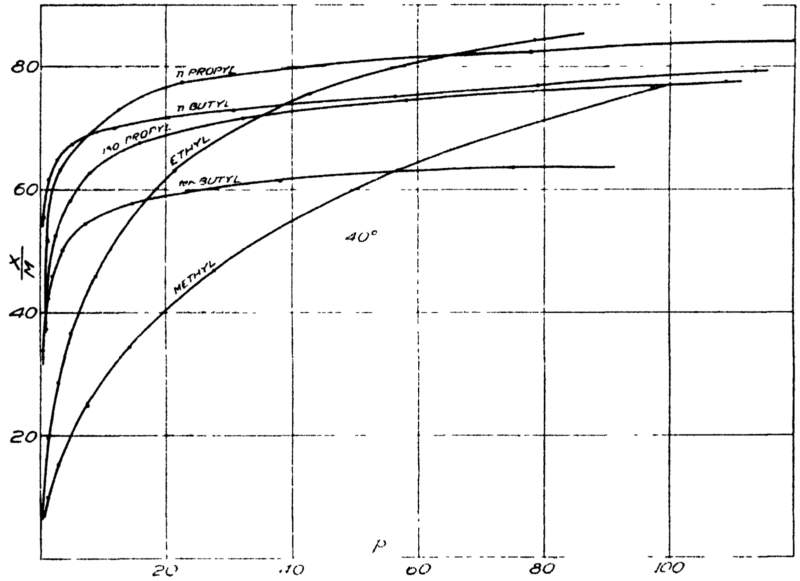

FIG. 2

The tendency for the isotherms to intersect upon variation of pressure is obvious from the plot given. The rapid increase in the adsorption of methyl chloride with increase in pressure is also particularly interesting. For pressures between 10 mm. and 20 mm. the volume of the normal alkyl chloride vapors adsorbed, (cc. per gram), decreases in the order ethyl, n-propyl, n-butyl, methyl. At pressures above 100 mm. the order becomes methyl, ethyl, n-propyl. Above this pressure the magnitude of the adsorption decreases with increase in the length of the carbon chain.

With rise in temperature the tendency for the isotherms to intersect becomes markedly less. For pressures below 60 mm., (Fig. 4) the volumes of vapor adsorbed at 99.5° increases as the length of the normal chain vapor molecule is increased. It is very probable that this relation is completely fulfilled at sufficiently high temperatures. This is also the order of increase in boiling points, critical temperatures and other physical properties of the liquids. At all temperatures the isotherms of the iso-propyl and tertiary butyl chlorides lie below those of the corresponding normal compounds.

The volume of each of the alkyl chloride vapors which had to be admitted to the charcoal at 0° before an equilibrium pressure could be detected is large. The volume of vapor adsorbed at low pressures (below 0.5 mm.), is greater the greater the molecular weight of the vapor. Thus, at 0° and under an equilibrium pressure of 0.45 mm. one gram of charcoal adsorbs 33.65 cc. of the tertiary butyl chloride and 12.99 cc. of ethyl chloride, while at the same temperature, but under 1.39 mm. only 7.85 cc. of methyl chloride are adsorbed.[7] These observations are even more striking when we take into consideration the fact that the total amount of vapor capable of being adsorbed decreases with increasing molecular weight. Further, the amount of vapor adsorbed at 0° under one mm. pressure is equal to or exceeds one-half of the total amount adsorbable at the same temperature under a pressure just short of saturation. This relation holds without exception for the five vapors studied.

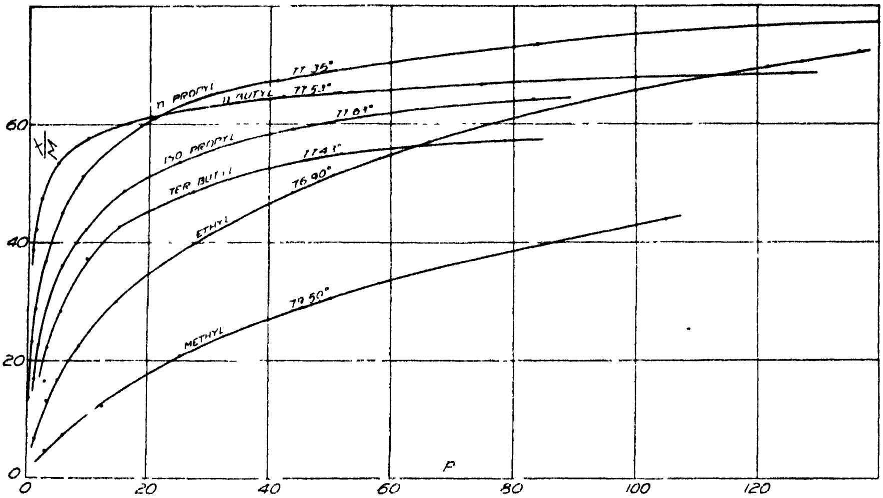

Fig. 3

It has been interesting to observe that the time necessary to attain adsorption equilibrium at a given temperature differs widely corresponding to different points on the isotherm. The time required is greatly increased in the pressure interval including the "break" of the isotherm; it is much greater for the iso-propyl and the tertiary butyl chlorides than for the normal compounds. In fact, it is difficult to reproduce the 0°-isotherm of the tertiary butyl chloride either in the pressure range including the break, or just below condensation. One illustration of the slowness of the pressure variation observed at the break point of the tertiary butyl chloride may not be amiss. Two and one-half hours after the admission of the vapor to the bulb the pressure over the charcoal was 30.65 mm. The pressure decreased slowly and regularly without exhibiting any sign of equilibrium even after 119 hours when the pressure was 19.50 mm. It was observed also that when the adsorption equilibrium was approached from the side of high pressure, especially, if the butyl chloride had been previously condensed on the charcoal, the values of X/M were always too high.

It is evident that the sluggishness in the attainment of adsorption equilibrium in this instance is due to steric hindrance. When the vapor is first admitted to the gas-free surface of the charcoal the molecules will be adsorbed on those points and areas most accessible to the vapor molecules. This will include also the most easily accessible points and areas on the capillary walls. With increase in the concentration and pressure of the vapor above the adsorbent there will be a crowding and a readjustment of the adsorbed molecules on the surface. These readjustments will require time and they will be most easily made on the more exposed charcoal surfaces; they will be more difficult within the capillaries where the influence of the size and shape of the vapor molecules will be more pronounced. We have then the phenomenon of a "drift," similar to that observed by Cude and Hulett[9] when thoroughly outgassed charcoal is immersed in liquids for long periods of time.

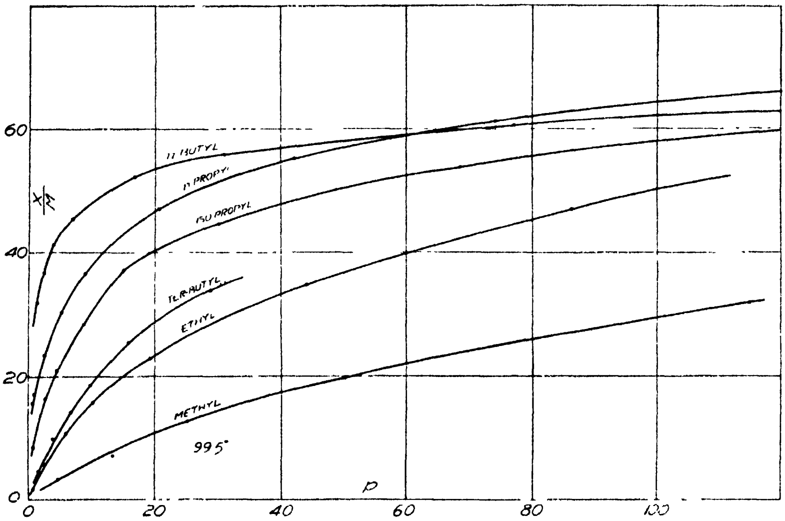

FIG. 4

The validity of the Freundlich equation, $X/m = \alpha.p^{1/n}$, requiresa constant value for the exponent $1/n$. The plot of the double-log isotherms should, if the equation applies to these vapors, give perfectly straight lines. The behavior of these isotherms is to be seen in Fig. 5. In general, the slopes, $1/n$, of these isotherms tend to become more constant the lower the temperature at which they are determined, and to a less pronounced extent also at higher pressures. The values of 1/n becomes smaller as the number of carbon atoms in the chain is increased. Further, the flaring of the isotherms, that is the variation of the log X/m values of the chain compounds with decreasing pressures, decreases with increase in the molecular weight of the vapor. This is exactly the same order as that previously observed for methane and its chlorine derivatives[7]. Further discussion of these isotherms will be left for a later paper.

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[9] Cude and Hulett: J. Am. Chem. Soc., 42, 391 (1920).

The effect of temperature on the adsorption of the monochlor alkyl derivatives is also shown by their isosteres. If the well-known relation,

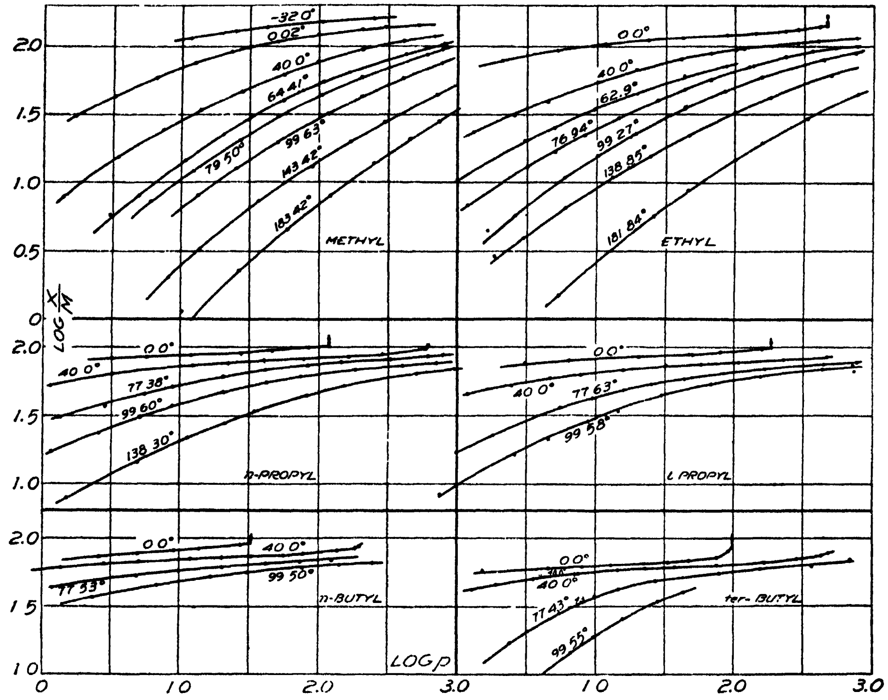

FIG. 5

$$\frac{d \ln p}{d\ 1/T} = -\frac{\Delta H}{R},$$

applies to adsorption phenomena, the slope of these isosteres should be proportional to the negative value of the heat of adsorption. Further, unless the heat of adsorption is dependent upon the temperature the isotherms should be parallel straight lines. Within limits of experimental error the isosteres are both parallel and rectilinear throughout the temperature range. Since they have the usual characteristic form we are omitting the graphs in order to save space. The heats of adsorption calculated from the mean slopes of all of the isosteres of each vapor are given in Table I.

TABLE I

Heats of Adsorption of the Vapors of Alkyl Chlorides on Charcoal

Vapor	ΔH cals.	Vapor	ΔH cals.
CH_3Cl	−8300	i-C_3H_7Cl	−12250
C_2H_5Cl	−10060	n-C_4H_9Cl	−13400
C_3H_7Cl	−12300	ter-C_4H_9Cl	−11600?

Upon the basis of theoretical considerations Coolidge[10] has justified the use of the Clausius-Clapeyron equation in the calculation of the heat evolved in the adsorption process. However, it has usually been found that the heat effect calculated in this way is lower than that experimentally determined. Pearce and McKinley[11] have determined the heat of adsorption of ethyl chloride and methyl chloride at 25°; the values obtained for ΔH were −15400 and −11600 cals., respectively. The liquids from which they obtained their vapors were those purified for the present work; their charcoal was taken from the same container and subjected to the same treatment in outgassing. The difference between the observed and calculated heats of adsorption may be due in part to the fact that in determining the heats of adsorption experimentally the vapors are not admitted to the charcoal under the equilibrium pressure.

Lamb and Coolidge[6] have shown that the heats of adsorption differ from the heats of vaporization by constant amounts. This they attribute to the compression caused by the adsorption forces. According to the Polanyi theory, however, the surface of the adsorbed layer increases in distance from the surface of the adsorbent as more and more vapor is adsorbed until, finally, it reaches the edge of the adsorption space. The potential and, therefore, the compressive forces decrease very rapidly very near the edge of the adsorption space, and hence the heat of compression must also decrease rapidly. In this range, therefore, the heat of adsorption should change very rapidly with the concentration until it becomes equal to the heat of vaporization.

Application of the Polanyi Theory

In his earlier work Polanyi[12] attempted to explain the forces existing between the adsorbent and adsorbed molecules. He assumed that the adsorption forces act through distances which are large compared with molecular diameters. Also, that the force exerted upon a molecule at a given distance from the surface of the adsorbent is independent of the temperature and independent of whether or not other molecules exist between the molecule and the surface. He has shown that for temperatures below 0.8 $T_{crit.}$ of the vapor the adsorption potential at any point in the adsorption space is given by the relation,

$$\epsilon_i = RT \ln \frac{p_s}{p_x},$$

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[10] Coolidge: J. Am. Chem. Soc., **48**, 1795 (1926).

[11] Pearce and McKinley: J. Phys. Chem., **32**, 360 (1928).

[12] Polanyi: Ber. deutsch. physik. Ges., **12**, 1012 (1924); Verh. deutsch physik. Ges., **18**, 55 (1916); Z. Elektrochemie, **26**, 370 (1920).

where p_s is the vapor pressure of the liquid in the free state and p_x is the equilibrium pressure in the adsorbed state. The potential ϵ_i is nothing more than the work done in transporting one mole of vapor from the saturation pressure, p_s to the equilibrium pressure p_x.

All points possessing the same adsorption potential, ϵ_i, form an equipotential surface. This and the surface of the adsorbent inclose a definite volume, —the adsorption space, ϕ_i. Assuming the adsorbed substance to have the same density as the free liquid, for temperatures well below the critical temperature, we can calculate the volume of the adsorption space from the relation,

$$\phi_i = x'/\delta,$$

where x' is x/m and δ is the density of the liquid. Thus, for every pair of p_x and x/m values we may calculate a pair of ϵ_i and ϕ_i values, so that

$$\epsilon_i = f(\phi_i).$$

The curves showing the potential distribution with the volume are given in Fig. 6.

The (ϵ ϕ)-curve is then a characteristic adsorption curve for a given vapor and adsorbent. If we assume with Polanyi that the temperature coefficient of the adsorption potential is zero, and make the necessary corrections for the volume occupied by the adsorbed substance, the curve should be the same for all temperatures. In the vicinity of and above the critical temperature corrections must be applied for the density of the adsorbed substance. By means of the thermal dilatation formula of the adsorbed substance as a liquid and of its equation of state as a vapor it is possible to calculate the adsorption isotherm at any other temperature from the (ϵ-ϕ)-curve determined for a single isotherm.

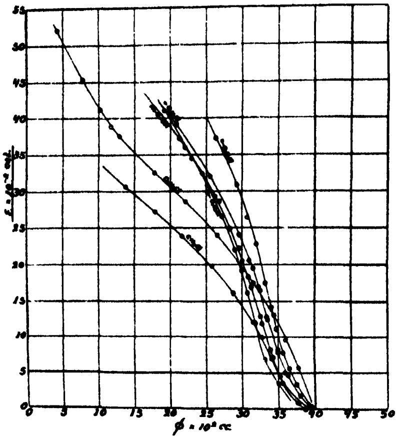

FIG. 6

We have calculated the (ϵ-ϕ)-curves for propyl chloride and iso-propyl chloride from both the 0° and 40° isotherms. In making these calculations the densities were taken from the "International Critical Tables" and they are corrected for temperature by the dilatation formulas given in the "Physical Chemistry Tables." The curves have been drawn for the 40° isotherms and the points calculated from the 0° isotherms are indicated by double circles. The agreement is all that can be desired. Berenyi[13] has previously applied the method here used to the data of Titoff for the adsorption of carbon dioxide. The agreement in this case is also most excellent.

The relative positions of the (ϵ-ϕ)-curves of the two pairs of isomers is interesting. While they do not coincide the curves for either pair of isomers run practically parallel throughout their whole extent. Further, for a given adsorption volume, ϕ, the adsorption potential, ϵ, of the normal compound, is greater than that of its isomer. Conversely, for equal adsorption potentials the adsorption space occupied is always greater for the normal compound. These curves show also the influence of lengthening the hydrocarbon chain by successive increments of CH_2. For relatively high values of ϵ, say ϵ = 3000 cals., the values of ϕ increase regularly from methyl chloride to n-butyl chloride. This relation disappears, however, as we approach saturation.

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[13] Berenyi: Z. physik. Chem., 94, 628 (1920).

It is interesting to note also that at the limit of the adsorption space, where the adsorption potential is zero, the adsorption volume, $\phi.10^2$, is practically the same for all of the vapors given, viz., about 39.5. This is almost identically the same value as that obtained by Pearce and Johnstone[7] for the adsorption of the chlorine derivatives of methane on charcoal from the same stock supply. The coincidence is exactly what we should expect, if the Polanyi theory involved is correct. The maximum value of ϕ would not necessarily be the same, however, on another sample of the same charcoal having a different degree of activation.

It is very probable that adsorption relations would be much more significant if comparisons were made at corresponding temperatures rather than at identical temperatures. We have in the 40° isotherms data which is quite suited for such a comparison. The boiling points of propyl chloride and tertiary butyl chloride are 46.6° and 51°, respectively; their isotherms are very similar in shape. We have calculated the ratio of the volumes of the two vapors adsorbed under the same pressure at different pressures throughout the pressure range from 3 mm. to 300 mm. The values of the ratios were found to be practically constant:

$$\frac{\text{cc. of propyl chloride vapor}}{\text{cc. of ter-butyl chloride vapor}} = \frac{1}{0.778} = 1.285$$

The molecular volumes of these chlorides as liquids at 40°, calculated from their values at 20°, are in the ratio

$$\frac{V_l\ \text{(propyl chloride)}}{V_l\ \text{(ter-butyl chloride)}} = \frac{90.7}{112.2} = \frac{0.823}{1}$$

If we now neglect the compressibility of the liquids, the small difference in boiling points, and also any possible blocking effect in the capillaries due to the larger cross-section of the tertiary butyl chloride molecules, we find that the ratio of the actual volumes of the adsorbed substances, considered as liquids, is

$$\frac{V_l\ \text{(propyl chloride)}}{V_l\ \text{(ter-butyl chloride)}} = \frac{1.06}{1.00}$$

Taking into consideration the uncertainty of the density data, this ratio of approximately unity should indicate that the amounts of different vapors, possessing a common orienting atom, adsorbed at identical, or nearly corresponding temperatures, occupy a definite volume for a given equilibrium pressure. It is our intention to study this relation more fully in a forthcoming study of the adsorption of vapors at their boiling points.

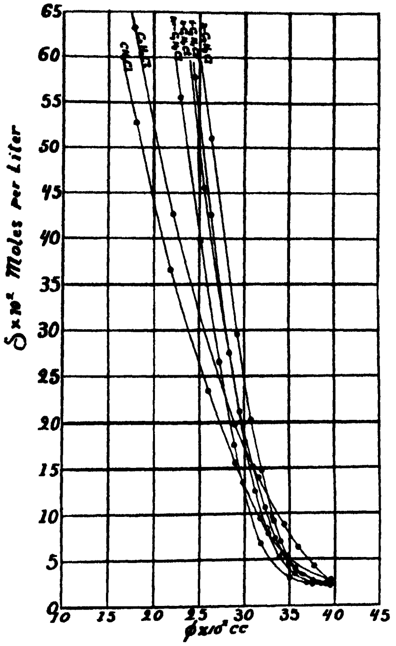

FIG. 7

In his calculations Polanyi has assumed that the density of the adsorbed vapor is the same as that of the free liquid at the same temperature. Above the critical temperature the density of the adsorbed substance is no longer equal to that of the liquid. In order to apply the characteristic (ϵ_i-ϕ_i) curves for the determination of an isotherm, Berenyi[18] has shown that it is necessary to make corrections for the change of density at the various levels in the adsorption space. The relation given by $\epsilon_i = g(\delta_i)$, indicates that for every potential level, ϵ_i, there is a corresponding density, δ_i. Making use of the equation of state of the adsorbed vapor, Berenyi finds that the relation between the density distribution and the potential can be expressed by the equation:

$$\frac{\epsilon_i}{RT} = \ln \frac{RT}{p_x\left(\frac{1}{\delta_i} - b\right)} - \frac{2a\delta_i}{RT} + \frac{1}{1 - b\delta_i} - 1,$$

where a and b are the van der Waal constants and δ_i is the density of the vapor at the potential level, ϵ_i. Neglecting the last three terms on the right will introduce only a negligible error, since $2a\delta_i/RT$ and $b\delta_i$ become vanishingly small at high temperatures. The application of this equation at the temperatures which we have used may introduce error in calculating the density distribution of the vapors studied. The values obtained for the different vapors, however, should be, relatively at least, of the correct order of magnitude. By elimination of ϵ_i between the two functions, $\epsilon_i = f(\phi_i)$ and $\epsilon_i = g(\delta_i)$, we obtain a relation between the density distribution and the volume, viz., $\delta_i = h(\phi_i)$. In making these calculations we have taken the constants a and b of the equations of state of the three lower alkyl chlorides from the Landolt-Börnstein-Roth Tabellen, Ed. 5. The constants for isopropyl chloride and the two butyl chlorides were not available in the literature. They were estimated from the values for similar compounds. The volume-density distribution relations thus obtained are shown graphically in Fig. 7.

Summary

1. The adsorption of the vapors of ethyl, n-propyl, isopropyl, n-butyl and tertiary butyl chlorides by charcoal has been determined at temperatures ranging from 0° to temperatures at which the vapors become unstable when in contact with charcoal. The stability of these alkyl chlorides toward heat decreases with increase in molecular complexity. The iso and tertiary compounds decompose at lower temperatures than do the corresponding normal compounds.

2. At low pressures and for all temperatures the volume of vapor adsorbed in the normal series increases with the molecular weight of the vapor. At 0° the order of adsorbability is completely reversed at sufficiently high pressures. At high temperatures (above 100°) the magnitude of the adsorption at all pressures increases with the length of the carbon chain. The adsorbability of the branch-chain compounds is at all temperatures and pressures less than that of the corresponding normal compounds. The influence of the branching structure of molecules upon the time required for the attainment of pressure equilibrium, especially at the break of the isotherm, is very pronounced.

3. The heats of adsorption of these vapors have been calculated from the slopes of the isosteres and they have been found to be lower than the values experimentally determined.

4. The potential distribution and the density distribution of the vapors in the adsorption space have been calculated according to the method of Polanyi.

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THE STATE OF FORMALDEHYDE IN AQUEOUS SOLUTIONS*

BY FREDERIC WALKER

Our present knowledge of the state of formaldehyde in aqueous solutions is based primarily upon the work of Auerbach and Barschall. As a result of an extensive study of the physical chemistry of such solutions, these investigators came to the conclusion that the solute was in the form of the simple hydrate, $CH_2O.H_2O$, plus a mixture of hydrated polymers having the general formula, $(CH_2O)_n.H_2O$. At concentrations up to approximately 34% they concluded that the only polymer present to any appreciable extent was the hydrated trimer, $(CH_2O)_3.H_2O$.

Auerbach and Barschall believed that the monomolecular hydrate of formaldehyde was methylene glycol, $CH_2(OH)_2$, whose methyl ether, methylal, $CH_2(OCH_3)_2$, is a well-known derivative of formaldehyde. According to this theory, the hydrated polymers of formaldehyde would be polymethylene glycols, having the general formula, $HO.(CH_2O)_n.CH_2OH$, similar to the polyethylene glycols, $(HO.(CH_2.CH_2.O)_n.CH_2.CH_2.OH)$, obtained when ethylene glycol is polymerized. As will be seen later, this view is now supported by the absorption spectra studies of S. A. Schou.

We have found that Auerbach's theories have been substantiated by the findings of later investigators and offer a workable theory for the interpretation of the physical behaviour of formaldehyde solutions. The object of this paper has been to review and correlate the scattered data on this subject. In doing this, we have discovered that the theories and data of Auerbach enable one to arrive at a quantitative explanation of the vapor pressure of formaldehyde in aqueous solutions as recently determined by Ledbury and Blair. We have shown that formaldehyde solutions follow Henry's law in that the partial pressure of the aldehyde vapor is proportional to the concentration of the solute in the simple monomolecular hydrate form. Finally we have been able to show by means of thermochemical calculations that the formaldehyde gas in equilibrium with aqueous solutions is probably the unhydrated monomolecular gas.

In recent years very little has been published on the physical chemistry of formaldehyde solutions. The standard books on formaldehyde scarcely mention it and the classic monograph published by Auerbach and Barschall in 1905 has now gone out of print. Since the use and importance of formaldehyde solutions has increased steadily throughout this period we are of the opinion that this would demand a thorough understanding of the reagent itself. Accordingly we shall begin our paper with a brief review of the research that has already been devoted to this subject.

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* Contribution from the Research Laboratory of The Roessler & Hasslacher Chemical Company.

Tollens and Mayer[1] in 1888 and Eschweiler and Grossmann[2] in 1890 first endeavored to measure the molecular weight of formaldehyde in aqueous solution and noticed a rather surprising anomaly. The apparent molecular weight of formaldehyde in a dilute solution prepared by diluting a more concentrated one was at first something over one and a half times the simple value of 30 required by the theory. If, however, the freezing point of the diluted solution was measured again after a day's standing, the normal value of 30 was obtained. From this evidence they concluded that concentrated formaldehyde solutions contained dissolved polymers which slowly dissociated on dilution.

In 1905 Auerbach and Barschall[3] made an extensive study of this phenomenon and determined the apparent molecular weight of formaldehyde in solutions of all concentrations up to approximately 38%. Their cryoscopic measurements for this work were all made in dilute solutions. This was possible because the change taking place on dilution in the case of most formaldehyde solutions was found to be very slow at 0°C. Accordingly they could dilute a sample of a concentrated formaldehyde solution in a measured volume of cold water and determine the apparent molecular weight of the formaldehyde in the concentrated solution from the freezing point of the dilute solution. Their results are shown in Table I.

TABLE I

The Apparent Molecular Weight of Formaldehyde in Aqueous Solutions at Room Temperature

	Volume Percent of CH_2O	Gms. CH_2O per 1000 gms. H_2O in the solution diluted for measurement	Freezing point lowering at the moment of dilution	Apparent molecular weight
1	2.39	24.3	1.497	30.0
2	5.99	20.0	1 140	32.5
3	11.54	39.13	1.999	36.2
4	15.81	54.15	2.600	38.5
5	21.36	36.15	1.555	43.0
6	24.20	41.15	1.705	44.6
7	25.76	43.83	1.805	44.9
8	30.60	52.4	2.001	48.45
9	37.38	64.56	2.24	53.3
10	37.71	65.2	2.25	53.6

From these data it may be seen that the apparent molecular weight of the formaldehyde molecules in solution increases with increasing concentration of formaldehyde. Since these measurements were all made under the same conditions and at approximately the same concentration the variation is most probably due to the association of solute molecules as the investigators believed.

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[1] Ber., **21**, 1566, 3503 (1888).

[2] Ann., **258**, 103 (1890).

[3] Monograph entitled, "Formaldehyde in wässriger Lösung", from Arbeiten aus d. Kaiserl. Gesundheitsamte, XXII, 3; Zentralblatt, **1905** II, 1081.

Having obtained these figures Auerbach sought for a simple mass action expression which would account for the data. He at first experimented with the equations shown below.

$$2\ CH_2O \rightleftarrows (CH_2O)_2 \qquad (I)$$
$$3\ CH_2O \rightleftarrows (CH_2O)_3 \qquad (II)$$
$$4\ CH_2O \rightleftarrows (CH_2O)_4 \qquad (III)$$
$$6\ CH_2O \rightleftarrows (CH_2O)_6 \qquad (IV)$$

The mass action constants based on these equations all showed unsatisfactory trends, the true state of affairs appearing to be something of a mean between equations II and III. For this reason he tried out the following equation in which the formaldehyde and polymer are shown to be hydrated.

$$3\ CH_2(OH)_2 \rightleftarrows CH_2OH.CH_2O.CH_2OH + 2\ H_2O \qquad (V)$$

The values obtained with this equation are shown in Table II compared with those obtained from equations II and III. These constants are here designated as K_{II}, K_{III} and K_V.

TABLE II

	Volume percent CH_2O	Apparent molecular weight	K_{II}	K_{III}	K_V
1	2.39	30.0	—	—	0.029
2	5.99	32.5	72	200	0.023
3	11.54	36.2	71	350	0.025
4	15.81	38.5	75	490	0.030
5	21.36	43.0	55	460	0.028
6	24.20	44.6	52	490	0.028
7	25.76	44.9	56	550	0.032
8	30.60	48.45	43	490	0.027
9	37.38	53.3	29	400	0.022
10	37.71	53.6	28	390	0.021
				Average K_V =	0.026

The values for K_V showed no trend and were constant within the limits of the experimental error. Accordingly the investigator was led to the belief that the formaldehyde in aqueous solutions was present as methylene glycol, $CH_2(OH)_2$, and the hydrated trimer, $C_3H_6O_3.H_2O$, in the state of equilibrium shown by the following mass action expression, in which the concentration of the various constituents is measured in terms of mols per liter.

$$K = 0.26 = \frac{(CH_2(OH)_2)^3}{(C_3H_6O_3.H_2O)(H_2O)^2} \qquad (1)$$

At higher concentrations it seemed probable that higher polymers were formed and the low values observed in the last two constants in the table were attributed to this.

Auerbach also showed that when paraformaldehyde was dissolved in cold water, the solute at first showed a high degree of polymerization which disappeared on standing. Apparently the polymerized formaldehyde dissolved as a polymer and then dissociated. Raising the temperature of formaldehyde solutions was found to decrease the polymerization.

M. Delépine[1] as a result of a thermochemical study of formaldehyde solutions in 1897, was led to conclusions that were in complete agreement with those of Auerbach.

Delépine found that on diluting concentrated aqueous solutions of formaldehyde there was an instantaneous evolution of heat followed by a slow absorption of heat. He further discovered that paraformaldehyde has a negative heat of solution. After a quantitative study of these phenomena, he came to the conclusion that the heat developed on diluting formaldehyde solutions was a normal heat of dilution while the heat gradually absorbed on standing was due to some internal change in the solution. The fact that paraformaldehyde possessed a negative heat of solution cast light on the nature of this internal change since paraformaldehyde was known to depolymerize on going into solution. Accordingly Delépine came to the belief that in concentrated formaldehyde solutions, the solute was partially polymerized and on dilution the polymerized molecules slowly dissociated. It is interesting to note that the heat first evolved was found to be practically equal to the heat gradually absorbed.

Delépine[2] also made a study of formaldehyde solutions in chloroform and benzene. In these solvents the compound dissolved but sparingly and the solutions resembled the solutions of permanent gases, whereas in the case of water the solubility is exceedingly high. This investigator measured the heat of solution of the dry gas in water and found it equal to 15 large calories, approaching the heat of formation of the energetic hydrates. This work led him to the conclusion that the aldehyde was hydrated in its aqueous solution.

The recent work of S. A. Schou[3] on the absorption spectra of formaldehyde solutions in water and hexane adds fresh support to these theories. Furthermore, these results show that the monomolecular hydrate of formaldehyde is probably methylene glycol, $CH_2(OH)_2$, and not $CH_2O.H_2O$. The absorption spectra of aqueous solutions of formaldehyde show the band spectra characteristic of the carbonyl group to such a slight extent that Schou was able to estimate that the ratio of CH_2O molecules to molecules of hydrate and polymer is at the most 1 to 1200. In hexane, however, the absorption spectra show that the solute is in the form of CH_2O. Schou checked this work by measurements made on trichloracetaldehyde whose hydrate, chloral, can be isolated.

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[1] Compt. rend. **124**, 816, 1454, 1528 (1897); Bull., (3) **17**, 849 (1897); Ann. Chim., (7) **15**, 554 (1898).

[2] Ann. Chim., (7) **15**, 530 (1898).

[3] J. Chim. phys., **26**, 72-76; Chem. Abs., **23**, 3438 (1929).

The absorption spectra of this compound in water and hexane were qualitatively identical to the formaldehyde spectra. A similar study of acetaldehyde showed that this compound was 26% in the form of $CH_3.CHO$ in aqueous solutions. It is most interesting to note that the heat of solution of acetaldehyde is approximately one third the heat of solution of formaldehyde.

In 1925, Ledbury and Blair[1] determined the vapor pressure of formaldehyde in aqueous solutions at a series of temperatures between 0° and 45°. The investigators published vapor pressure curves and presented an empirical formula for calculating the vapor pressure of formaldehyde in aqueous solutions within the limits of their data.[2] This formula involved two constants, one of which varied with concentration.

The partial pressure of formaldehyde in aqueous solutions as seen in these curves showed a pronounced negative deviation from Raoult's Law. Henry's law for solutions at 20° was followed up to concentrations of approximately 4% after which a negative deviation became increasingly apparent. As will now be shown, a comparison of these data with Auerbach's findings for solutions at room temperature showed that the vapor pressure of formaldehyde was proportional to the mol fraction of methylene glycol. The fact that dissolved formaldehyde is wholly in the methylene glycol form up to concentrations of approximately 4% accounts for the agreement with Henry's law in this range.

Since the solute molecules found in formaldehyde solutions have the general formula, $(CH_2O)_n.H_2O$, the total number of molecules in these solutions does not vary with the concentration. Accordingly if G is taken as equal to the number of grams of formaldehyde in 100 grams of solution, the mol fraction of methylene glycol in dilute solutions may be expressed as follows:

$$x_{CH_2(OH)_2} = \frac{\frac{G}{30}}{\frac{100-G}{18}} = 0.60\,\frac{G}{100-G}$$

Now taking γ as equal to the fraction of dissolved formaldehyde in the methylene glycol form, we may write the following expression for the mol fraction of methylene glycol at all concentrations.

$$x_{CH_2(OH_2)} = 0.60\,\frac{\gamma G}{100-G}$$

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[1] J. Chem. Soc., **127**, 26-40, 2832-2839 (1925).

[2] The formula developed by these investigators is as follows:

$$\log_{10}P_{CH_2O} = \alpha - 2905/T$$

The value of α varies with the concentration and has the following values:

α 10% = 9.47
α 20% = 9.70
α 30% = 9.81
α 40% = 9.87

We have found that this formula gives approximately correct values for the vapor pressure of formaldehyde up to 100° by comparing the calculated values of the vapor pressure with those found by Auerbach.

Hence if the vapor pressure of formaldehyde in aqueous solutions is proportional to the mol fraction of methylene glycol alone, the following modified Henry's law expression should hold true.

$$P_{CH_2O} = K^1 \frac{\gamma G}{100\text{-}G} \tag{2}$$

Auerbach determined the apparent molecular weight of formaldehyde in solutions of various concentrations from which the corresponding γ values were easily calculated. By inserting these figures together with the values for the partial pressure of formaldehyde obtained from a curve based on the data of Ledbury and Blair for solutions at 20° in which the vapor pressure was plotted as a function of concentration in terms of weight percent, we were able to calculate values of K^1 for the equation.

In the following table are shown values of γ found from Auerbach's data for solutions of various concentrations, and the values of K^1 calculated therefrom. For purposes of comparison we have also included values for the unmodified Henry's law constant, K_H which were calculated by means of the equation shown below.

$$P_{CH_2O} = K_H . X_{CH_2O} = \frac{3G}{500\text{-}2G} \tag{3}$$

TABLE III

Values of K^1 and γ for solution of formaldehyde at 20°C.

G	P_{CH_2O} In millimeters of mercury	γ Observed Calculated from Auerbach's data	K^1	K_H
2.4	0.11	0.98	4.6	7.5
5.9	0.24	0.87	4.4	6.8
11.2	0.39	0.72	4.3	5.6
14.7	0.49	0.64	4.5	5.2
21.1	0.61	0.53	4.3	4.4
22.6	0.67	0.49	4.7	4.5
24.0	0.70	0.48	4.6	4.4
28.2	0.80	0.41	5.0	4.1
33.8	0.93	0.33	5.5	4.0
		Average K^1 =	4.5	

As will be seen the values thus obtained for K^1 are practically constant. They show a slight trend at concentrations over 28%. This may be accounted for as due to the appearance of small quantities of higher polymers at these concentrations. Furthermore the experimental error in the data is greater at the higher concentrations.

The vapor pressure of formaldehyde in aqueous solutions at 100° was determined by Auerbach. At this temperature the solutions still show a negative deviation from Raoult's law but Henry's law is followed up to concentrations of approximately 22%. This is in agreement with Auerbach's finding that when the temperature is raised the equilibrium is shifted in the direction of methylene glycol and the fraction of formaldehyde in the form of hydrated polymers is decreased. With these data we were able to calculate the value of K^1 in equation (2) since at concentrations below 22%, γ is equal to one. Using this value of K^1 we were then able to calculate the γ values for solutions at higher concentrations by substituting in the same equation and solving for γ^1. These results are shown in the following table. The values for $100\text{-}G/G.P_{CH_2O}$ are given which are equal to K^1 at the lower concentrations but fall off as γ decreases.

TABLE IV

Formaldehyde Solutions at 100°

G	P_{CH_2O} In millimeters of mercury	$100-G/G \,.\, P_{CH_2O}$	γ
7.69	28.3	340	1.00
14.29	56.5	339	1.00
20.00	85.0	340	1.00
22.1	96.0	339	1.00
25.0	106.8	320	0.94
26.8	110.0	300	0.88
29.4	103.0	249	0.73
31.8	94.2	202	0.59
34.4	106.3	199	0.59

K^1 at 100° = 340

We have thus far said nothing about the state of formaldehyde in the vapor phase in equilibrium with aqueous solutions. Some investigators have believed that this vapor consisted of varying proportions of the molecular species CH_2O, $(CH_2O)_n$, $CH_2(OH)_2$ and $(CH_2O)_n.H_2O$. That hydrated polymers should exist in the vapor phase to any extent now seems unlikely since the concentration of these polymers in aqueous solution has no appreciable influence on the vapor pressure. That unhydrated polymers should exist also seems unlikely since Auerbach and Plüddemann[1] found that these were unstable in the presence of water vapor and tended to dissociate under its influence. The only two species of formaldehyde gas which have been studied in a pure state are the monomolecular gas,[2] CH_2O, obtained by the vaporization of the "trioxymethylene" of commerce and a trimeric gas[3] obtained by the vaporization of α-trioxymethylene, a rare polymer obtained only by special procedures. These facts made it seem probable that the formaldehyde gas in equilibrium with aqueous solutions was either the simple monomeric variety or methylene glycol vapor.

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[1] **Zentralblatt, 1914, I,** 956.

[2] **Trautz and Ufer: J. prakt. Chem., (2) 113,** 105 (1926).

[3] **Pratesi: Gazz., 14,** 139 (1884).

Now the constant for the Henry's law expression for formaldehyde would also be the mass action constant for the following equation:

$$CH_2(OH)_2 \text{ (in solution)} \rightleftarrows 1 \text{ mol formaldehyde gas} + \Delta H \qquad (A)$$

Assuming that the formaldehyde gas is CH_2O or $CH_2(OH)_2$ and writing the equation in the opposite direction we obtain the following:

$$CH_2O_{(gas)} \text{ or } CH_2(OH)_{2(gas)} + Aq. \rightleftarrows CH_2(OH)_{2(\text{in solution})} + \Delta H \qquad (B)$$

Here we can see that ΔH is the heat of solution of the formaldehyde gas that is in equilibrium with aqueous formaldehyde.

Delépine determined this value by measuring the heat evolved when anhydrous formaldehyde gas was dissolved in water. He thus obtained a value of 15,000 calories.[1] H. v. Wartenburg recently determined the heat of formation of anhydrous, gaseous formaldehyde to be 28,700 calories[2] and if this is subtracted from Delépine's figure for the heat of formation of formaldehyde in aqueous solution (40,400 calories[1]), we obtain another value for ΔH. This value is 11,700 calories. Since we knew the Henry's law constants for formaldehyde solutions at 20° and 100°, we were able to calculate an approximate value for ΔH in equation (B). This was done by substituting the T and K values in the following equation in which it is assumed that ΔH does not vary with temperature.

$$\log_e \frac{K_2}{K_1} = \frac{H(T_1 - T_2)}{R\,T_1\,T_2} \qquad (4)$$

$$2.30 \log \frac{340}{4.6} = \frac{80\,\Delta H}{216,000}$$

$$\Delta H = -\frac{2.30 \times 1.869 \times 216,000}{80} = 11,600 \text{ calories}$$

As a check on this value we also determined the Henry's law constant for formaldehyde solutions at 45°C. and used it in the calculation of ΔH. The value for the Henry's law constant at 45°C. was obtained from the data of Ledbury in the same manner that the constant for 100° was obtained from the data of Auerbach. The results are shown in Table V in which the vapor pressure values have been obtained from a curve based on Ledbury's data in which the vapor pressure was plotted as a function of formaldehyde concentration in terms of weight percent.

On substituting this value for K^1 in equation (4) together with the value for the 20° constant, we obtained a value for ΔH of $-12,300$ calories. Since the two thermochemical values were approximately equal, we concluded that our previous assumption had been correct. ΔH did not vary appreciably

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[1] Delépine: Compt. rend., **124**, 816 (1897).

[2] H. v. Wartenburg: Z. angew, Chem., **38**, 591-2 (1925).

TABLE V

Formaldehyde Solutions at 45°.

G	P_{CH_2O} In millimeters of mercury	$100-G/G \cdot P_{CH_2O}$	γ
2	0.50	24.5	1.00
4	0.97	24.7	1.00
6	1.40	21.9	0.89
8	1.83	21.1	0.86
10.4	2.30	19.8	0.81
	K^1 at 45°	= 24.6	

with temperature and was equal to approximately −12,000 calories. This value of ΔH makes it seem possible that the formaldehyde gas in equilibrium with aqueous solutions consists of monomeric unhydrated molecules. If this gas were a formaldehyde polymer or methylene glycol vapor we should certainly expect a much lower value. ΔH in the latter case would have been a simple heat of solution. The vapor pressure of formaldehyde over its aqueous solutions is probably the decomposition pressure of the dissolved methylene glycol. The extraordinary influence of temperature on the partial pressure of formaldehyde in aqueous solutions adds weight to this conclusion The vapor pressure of water at 100° is 44 times its value at 20° whereas the partial pressure of formaldehyde in a 15% aqueous solution at 100° is 115 times its value at 20°.

In concluding we would point out that the escaping tendency of formaldehyde molecules in aqueous solution is manifested in two ways, by the vapor pressure of gaseous formaldehyde and by the polymerization of the dissolved molecules. The hydrated trimer is fairly soluble but as the polymerization increases the solubility decreases and paraformaldehyde, $(CH_2O)_n.H_2O$, is precipitated. At high temperatures the formaldehyde escapes, as a gas, at low temperatures as a precipitate.

Summary

1. The work of previous investigators has shown that in aqueous solutions of formaldehyde, the solute is probably in the form of the simple hydrate, methylene glycol, $CH_2(OH)_2$, plus a mixture of hydrated polymers having the general formula, $(CH_2O)_n.H_2O$. The evidence upon which this statement is based consists of vapor pressure data, cryoscopic data, thermochemical data and a study of the absorption spectra of formaldehyde solutions.

2. According to Auerbach the only polymer present to any appreciable extent in formaldehyde solutions up to concentrations of approximately 38% is the hydrated trimer, $(CH_2O)_3.H_2O$. The methylene glycol in these solutions is in chemical equilibrium with this hydrated polymer. Raising the temperature of the solution or lowering the concentration of formaldehyde shifts the

equilibrium in the direction of methylene glycol. This statement rests primarily upon the cryoscopic data of Auerbach but the writer has found that it is in agreement with Ledbury's vapor pressure data as seen below.

3. The writer has found that formaldehyde solutions obey Henry's law in that the partial pressure of the aldehyde is proportional to the concentration of the solute in the methylene glycol form. This has been shown to be the case for solutions up to 34%. The data used were Auerbach's cryoscopic data in conjunction with Ledbury's vapor pressure data for formaldehyde solutions at 20°C.

4. According to the writer the formaldehyde in the vapor in equilibrium with aqueous solutions of formaldehyde is probably monomolecular unhydrated formaldehyde gas. The writer came to this conclusion through thermochemical considerations based on a comparison of the thermochemical data of Delépine and thermochemical calculations carried out with the Henry's law constants calculated for aqueous formaldehyde solutions at various temperatures.

OXIDATION OF CARBOHYDRATES AND FATS BY AIR IN PRESENCE OF YELLOW PHOSPHORUS

BY SACHINDRA NATH CHAKRAVARTI AND N. R. DHAR

In previous communications[1] from this laboratory, the phenomenon of induced oxidation has been extensively investigated. It has been shown that solutions of carbohydrates, fats, etc., which cannot be oxidised under ordinary conditions can very easily be oxidised at the laboratory temperature if a current of air is passed through the solution in presence of substances like ferrous hydroxide, cerous hydroxide, manganous hydroxide, sodium sulphite, etc. It has been shown that these easily oxidisable substances in course of their own oxidation by air induce or promote the oxidation of other substances (carbohydrates, fats, etc.) which have the potentiality of being oxidised under ordinary conditions. In a recent paper[2] Dhar has advanced an explanation of the induced reactions based on the generation of ions in chemical changes. It is well known that ions are generated in the oxidation with phosphorus. It is very likely that these ions activate the molecules of oxygen which thus becomes reactive and induce chemical changes which are not possible with molecular oxygen. It is well known that the oxidation of phosphorus can be retarded by various substances. Thénard was the first to observe that the oxidation of phosphorus is considerably decreased by the presence of some organic vapours.[3] Graham[4] observed that alcohol vapour, ether, ethylene, naphtha, sulphuretted hydrogen, etc., protected phosphorus from being acted upon by oxygen. Thus these organic substances act as negative catalysts in the oxidation of phosphorus.

Having investigated a large number of such reactions in which the oxidation of one substance is retarded by the presence of a negative catalyst, Dhar[5] has put forward the view that the phenomenon of negative catalysts is possible when the catalyst itself is likely to be oxidised. Thus in every case of such negative catalysis, the catalyst simultaneously gets oxidised. Though sodium arsenite does not get oxidised under ordinary conditions by passing air through the solution, it can be oxidised under the same conditions only if it is mixed with sodium sulphite or any other reducing agent. At the same time, the oxidation of sodium sulphite is retarded. Hence it was expected that as the oxidation of phosphorus is retarded by the presence of some organic substances, it seems likely that these inhibitors also will get oxidised along with the slow oxidation of phosphorus. The present investigation was undertaken with a view to observe whether phosphorus can be used as a suitable inductor like sodium sulphite, ferrous hydroxide, cerous hydroxide, etc. Also, as phosphorus gets oxidised with the generation of ions, it was expected that it would prove a very good inductor. The experimental results recorded in the following pages show that these expectations have been realised to a certain extent.

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[1] J. Chem. Soc., **111**, 690 (1917); Z. anorg. Chem., **122**, 146 (1922); J. Phys. Chem., **29**, 376, 799 (1925); **30**, 939 (1926); **32**, 1663 (1928).

[2] J. Phys. Chem., **28**, 948 (1924).

[3] "Traité de chimie," **1**, 236 (1816).

[4] Quarterly Journal of Science, **11**, 83 (1829).

[5] Proc. K. Akad. Weten. Amsterdam, **29**, 1923 (1921).

Experimental

Phosphorus was cut into small bits (each bit being approximately 0.005 gm.) and put in water. The solutions of carbohydrates or the potassium salts of fatty acids were added to it and the volume made up to 100 cc. Dry air free from carbon dioxide was passed through the bottles, care being taken that the air came in contact with the phosphorus surface. A blank experiment was also conducted to see if diffused light of the laboratory had any effect on the oxidation. The fumes of the oxides of phosphorus which were generated from the bottle containing phosphorus, were passed through the same quantity of the solutions of carbohydrates or other substances. The residual carbohydrates were estimated by their reduction of Fehling's solution, the precipitated oxide of copper being dried, ignited, and weighed. The oleate, stearate, and palmitate were estimated by their absorption of iodine monochloride, before and after the experiment. The oxalate and the oxalic acid were estimated by precipitation as calcium oxalate and subsequent titration with potassium permanganate in presence of acetic acid which dissolved the precipitate of calcium phosphite and phosphate. The results are given in Tables I-IV.

TABLE I

Carbohydrates and Bits of Phosphorus
Amount of phosphorus 4.0 gm (Each bit = 0.005 gm)
Amount of carbohydrates 0.1 gm.
Time $5\frac{1}{2}$ hours
Temperature 34°

Carbohydrates	Percentage of oxidation in the diffused light of the laboratory (1)	Percentage of oxidation in presence of Phosphorus (2)	Percentage of oxidation in presence of Phosphorus only (3)	Percentage of oxidation in presence of fumes of Phosphorus (4)	Percentage of oxidation in presence of fumes only (5)
Starch	2.9%	6.1%	3.2%	3.5%	0.6%
Maltrose	2.7%	4.4%	1.7%	3.1%	0.4%
Dextrose	1.9%	4.5%	2.6%	2.5%	0.6%
Glucogen	2.1%	4.9%	2.8%	2.7%	0.6%
Inulin	1.8%	4.4%	2.6%	2.3%	0.5%
Lactose	1.8%	3.9%	2.1%	2.2%	0.4%
Fructose	1.7%	3.9%	2.2%	2.1%	0.4%
Glucose	1.7%	4.2%	2.5%	2.2%	0.5%
Sucrose	1.6%	4.7%	3.1%	2.2%	0.6%
Galactose	1.1%	3.7%	2.6%	1.6%	0.6%
Arabinose	0.8%	3.2%	2.4%	1.3%	0.5%

TABLE II

Fatty Substances and Bits of Phosphorus

Amount of phosphorus 4.0 gm (Each bit = 0.005 gm)
Amount of fatty substance 0.1 gm
Time 5½ hours
Temperature 34°

Fatty Substances	(1)	(2)	(3)	(4)	(5)
Potassium oleate	2.6%	6.7%	4.1%	3.9%	0.8%
Potassium stearate	2.8%	7.3%	4.5%	3.7%	0.9%
Potassium palmitate	2.1%	6.1%	4.0%	2.9%	0.8%
Potassium oxalate	1.6%	5.6%	4.0%	2.9%	0.8%
Oxalic acid	1.4%	4.9%	3.5%	2.1%	0.7%

TABLE III

Carbohydrates and Bits of Phosphorus

Amount of phosphorus 4.0 gm (Each bit = 0.005 gm)
Amount of carbohydrates 0.01 gm
Time 11 hours
Temperature 36°

Carbohydrates	(1)	(2)	(3)	(4)	(5)
Starch	5.4%	11.3%	5.9%	6.6%	1.2%
Maltose	5.1%	8.1%	3.0%	5.7%	0.6%
Dextrin	3.8%	8.7%	4.9%	4.8%	1.0%
Glycogen	3.8%	9.2%	5.9%	4.8%	1.0%
Inulin	3.7%	9.0%	5.3%	4.7%	1.0%
Lactose	3.4%	7.4%	4.0%	4.2%	0.8%
Fructose	3.2%	7.2%	4.0%	4.0%	0.8%
Glucose	2.9%	7.7%	4.8%	3.8%	0.9%
Sucrose	2.9%	8.8%	5.9%	4.1%	1.2%
Galactose	2.0%	6.8%	4.8%	3.0%	1.0%
Arabinose	1.4%	5.9%	4.5%	2.3%	0.9%

TABLE IV

Fatty Substances and Bits of Phosphorus

Amount of phosphorus 4.0 gm (Each bit = 0.005 gm)
Amount of fatty substances 0.1 gm
Time 11 hours
Temperature 34°

Fatty Substances	(1)	(2)	(3)	(4)	(5)
Potassium oleate	4.4%	11.7%	7.3%	5.8%	1.4%
Potassium stearate	5.1%	13.1%	8.0%	6.7%	1.6%
Potassium palmitate	4.0%	10.9%	6.9%	5.4%	1.4%
Potassium oxalate	3.0%	10.0%	7.0%	4.4%	1.4%
Oxalic acid	2.3%	9.1%	6.8%	3.6%	1.3%

A second set of experiments was started in exactly the same way, the only difference being that instead of small bits of phosphorus, colloidal phosphorus was prepared in the following way. About two grams of phosphorus were taken in 25 cc. of absolute alcohol in a small stoppered bottle and warmed in a water bath until the phosphorus melted. The bottle was vigorously shaken and in a short time the phosphorus was divided into very fine particles. The process was repeated several times so that a saturated solution of phosphorus was obtained. The solution was poured into water and a milky white emulsion was formed. In this way, a suspension of about 0.1 gm. of phosphorus was obtained. The next procedure was exactly similar to the previous ones. The oxidation of oleate, stearate, and palmitate could not be investigated in this particular case as the alcohol present interfered with the method of estimation followed in the case of these substances, by absorbing a large quantity of iodine. The oxalate was estimated by adding calcium chloride and dissolving the precipitated phosphates and phosphites by acetic acid and estimating the calcium oxalate with potassium permanganate. The other methods of estimation were similar to the previous ones. The results are tabulated in Tables V-VIII.

TABLE V

Carbohydrates and Colloidal Phosphorus
Amount of phosphorus 0.1 gm
Amount of carbohydrates 0.1 gm
Time 5½ hours
Temperature 36°

Carbohydrates	(1)	(2)	(3)	(4)	(5)
Starch	3.2%	8.8%	5.6%	4.3%	1.1%
Maltose	3.0%	6.3%	3.3%	3.7%	0.7%
Dextrin	2.1%	6.9%	4.4%	3.0%	0.9%
Glucogen	2.2%	7.1%	4.9%	3.2%	1.0%
Inulin	2.1%	6.9%	4.8%	3.1%	1.0%
Lactose	2.0%	6.0%	4.0%	2.8%	0.8%
Fructose	2.0%	6.4%	4.4%	3.1%	1.1%
Glucose	2.0%	6.5%	4.5%	2.9%	0.9%
Sucrose	1.9%	7.4%	5.5%	3.0%	1.1%
Galactose	1.3%	6.0%	4.7%	2.2%	0.9%
Arabinose	1.2%	5.5%	4.3%	2.2%	1.1%

TABLE VI

Oxalates and Colloidal Phosphorus
Amount of phosphorus 0.1 gm
Amount of oxalates 0.1 gm
Time 5½ hours
Temperature 36°

Substances	(1)	(2)	(3)	(4)	(5)
Potassium oxalate	1.9%	7.0%	5.1%	2.9%	1.0%
Oxalic acid	1.6%	6.4%	4.8%	2.5%	0.9%

TABLE VII

Carbohydrates and Colloidal Phosphorus
Amount of phosphorus 0.1 gm
Amount of carbohydrates 0.1 gm
Time 11 hours
Temperature 36°

Carbohydrates	(1)	(2)	(3)	(4)	(5)
Starch	5.4%	11.0%	5.6%	6.6%	1.2%
Maltose	5.2%	8.5%	3.3%	5.9%	1.7%
Dextrin	3.9%	8.8%	4.9%	4.8%	0.9%
Glycogen	3.9%	9.0%	5.1%	4.1%	1.2%
Inulin	3.9%	8.9%	5.0%	4.9%	1.0%
Lactose	3.3%	7.3%	4.0%	4.0%	0.7%
Fructose	3.1%	7.2%	4.1%	3.9%	0.8%
Glucose	3.0%	7.6%	4.6%	4.0%	1 0%
Sucrose	2.8%	8.3%	5.5%	4.0%	1.2%
Galactose	2.2%	7.0%	4 8%	3.2%	1.0%
Arabinose	1.4%	5.8%	4.4%	2.2%	0.8%

TABLE VIII

Oxalates and Colloidal Phosphorus
Amount of phosphorus 0.1 gm
Amount of oxalate 0.1 gm
Time 11 hours
Temperature 36°

Substances	(1)	(2)	(3)	(4)	(5)
Potassium oxalate	3.2%	8.6%	5.2%	4.2%	1.0%
Oxalic acid	2.6%	7 7%	5.1%	3.6%	1.0%

A third set of experiments was conducted under similar conditions but this time finely divided phosphorus (almost powdered) was taken as the inductor. Finely divided phosphorus was prepared in the following way. Two grams of phosphorus were taken in about 30 cc. of water in a stoppered bottle and kept in a water bath until the phosphorus just melted. The bottle was shaken vigorously and in a short time, the phosphorus solidified but in very fine particles—almost to a powdery form. The advantage in working with this form of phosphorus was that on slightly agitating this phosphorus in water, a portion of it remained in a suspended condition temporarily, so when air was passed through such a mixture, a larger volume of air came in contact with the surface of the phosphorus than in the case of small bits of phosphorus.

The next step and the methods of estimation were similar to the other ones. The results are tabulated in Tables IX-XII.

Table IX

Carbohydrates and finely divided Phosphorus

Amount of phosphorus 2.0 gm
Amount of carbohydrates 0.1 gm
Time 5½ hours Temperature 34°

Carbohydrates	(1)	(2)	(3)	(4)	(5)
Starch	3.1%	14.7%	11.6%	5.3%	2.2%
Maltrose	2.8%	9.4%	6.6%	4.1%	1.3%
Dextrin	2.0%	11.0%	9.0%	3.8%	1.8%
Glycogen	2.2%	12.0%	9.8%	4.1%	1.9%
Inulin	2.0%	11.4%	9.4%	3.9%	1.9%
Lactose	1.9%	9.9%	8.0%	3.5%	1.6%
Fructose	1.8%	10.0%	8.2%	3.4%	1.6%
Glucose	1.8%	10 8%	9.0%	3.6%	1.8%
Sucrose	1.8%	12.4%	10.6%	4.0%	2.2%
Galactose	1.2%	10.2%	9.0%	3.0%	1.8%
Arabinose	1.0%	9 6%	8.6%	2.7%	1.7%

Table X

Fatty Substances and finely divided Phosphorus

Amount of phosphorus 2.0 gm
Amount of fatty substances 0.1 gm
Time 5½ hours Temperature 36°

Fatty Substances	(1)	(2)	(3)	(4)	(5)
Potassium oleate	2.4%	11.7%	9.3%	4.2%	1.8%
Potassium stearate	2 8%	13 9%	11.1%	5 0%	2.2%
Potassium palmitate	2 3%	11.2%	8.9%	4.1%	1.8%
Potassium oxalate	1.6%	9.2%	7.5%	3.1%	1.5%
Oxalic acid	1.3%	8.5%	7.2%	2 7%	1.4%

Table XI

Carbohydrates and finely divided Phosphorus

Amount of phosphorus 2 0 gm
Amount of carbohydrates 0.1 gm
Time 11 hours Temperature 34°

Carbohydrates	(1)	(2)	(3)	(4)	(5)
Starch	5.4%	22.2%	16.8%	8.7%	3.3%
Maltose	5.2%	15.1%	9.9%	7.2%	2.0%
Dextrin	3.8%	17.6%	13 8%	6.5%	2.7%
Glycogen	3.8%	18.4%	14 6%	6.7%	2.9%
Inulin	3.8%	18.2%	14.4%	6.7%	2.9%
Lactose	3.3%	15.3%	12.0%	5.7%	2.4%
Fructose	3.2%	15.5%	12.3%	5.7%	2.5%
Glucose	3.0%	16.5%	13.5%	5.7%	2.7%
Sucrose	2 9%	19.4%	16.5%	6.2%	3.3%
Galactose	2.1%	15.9%	13.8%	4.8%	2.7%
Arabinose	1.4%	14.3%	12 9%	4.0%	2.6%

TABLE XII

Fatty Substances and finely divided Phosphorus
Amount of phosphorus 2.0 gm
Amount of fatty substances 0.1 gm
Time 11 hours
Temperature 36°

Fatty Substances	(1)	(2)	(3)	(4)	(5)
Potassium oleate	4.7%	22.1%	17.4%	8.2%	3.5%
Potassium stearate	5.3%	26.5%	21.2%	9.5%	4.2%
Potassium palmitate	4.2%	21.0%	16.8%	7.5%	4.3%
Potassium oxalate	3.0%	17.1%	14.1%	5.8%	2.8%
Oxalic acid	2.4%	16.2%	13.8%	5.1%	2.7%

From the foregoing data it is quite clear that phosphorus can be used as an inductor in the oxidation of carbohydrates and fats. Another interesting fact is observed that even the fumes given off in the oxidation of phosphorus can induce the oxidation of those substances to a slight extent. This probably is caused by particles of phosphorus or phosphorus trioxide which are likely to be carried away by the air. As these experiments were conducted at a time when the intensity of sunlight was very strong, even the diffused light of the laboratory could oxidise a certain portion of the substances. Making allowance for the oxidation in the diffused light without any inductor, we find that phosphorus in the finely divided state induced the oxidation of carbohydrates and fatty substances to the greatest extent. Colloidal phosphorus comes next and then the bits of phosphorus. Of course colloidal phosphorus having the largest surface should have been the most reactive amongst the three varieties but as it was prepared from an alcohloic solution, the alcohol present retarded the oxidation very much. Moreover, as the amount of phosphorus available in the colloidal phosphorus was very small being only about 0.1 gm. per experiment it was oxidised in a very short time. This is the reason why the oxidation of the carbohydrates and the fatty substances in presence of colloidal phosphorus as recorded in the present paper does not show change with time. Thus the amount of oxidation in 10 hours is almost the same as the amount of oxidation in 5 hours. If however, phosphorus could be suspended in water in some other way without introducing any other foreign matter, other than the inductor and the acceptor, it is likely that the percentage of oxidation would be much higher.

From the tables it would be apparent that in each case, starch is oxidised to the highest extent. Curiously enough, in all our previous communications on induced reactions with different carbohydrates we have found that starch can be very easily oxidised. We have shown in a recent communication that in these slow oxidations complete oxidation of carbohydrates, fats and nitrogenous substances to carbon dioxide takes place, without the formation of intermediate products. Hence, it is rather surprising how the complex molecule of starch is so easily susceptible to oxidation, whereas, glucose which is much simpler in structure, can not be so easily oxidised. This much is quite certain that in slow photochemical or induced oxidations, starch does not pass through the stage of glucose before its oxidation to carbon dioxide.

In the oxidation of carbohydrates in presence of diffused light we find that the order in which they are oxidised are as follows:—

Starch > maltose > dextrin > glycogen > inulin > lactose > fructose > glucose > sucrose > galactose > arabinose.

The order is exactly the same as has been recorded in the case of the oxidation in presence of sunlight without any inductor. However, the order is different in the case of the oxidation in presence of phosphorus. The order of the oxidation of carbohydrates in presence of each variety of phosphorus is the same and is as follows:—

Starch > sucrose > glycogen > inulin > dextrin > galactose > glucose > arabinose > fructose > lactose > maltose.

Almost the same order follows in the oxidation in presence of the fumes of phosphorus and phosphorous trioxide.

In the oxidation of the fatty substances, the oxidation follows the same order in all the three types that have been investigated and also the same order as in the diffused light.

Stearate > oleate > palmitate > oxalate > oxalic acid.

It appears also that finely divided phosphorus has the greatest power of inducing the oxidation. The next in order comes colloidal phosphorus in presence of alcohol and last the coarsely divided phosphorus.

In a foregoing paper we have shown that when a mixture of finely divided sulphur and phosphorus are kept under water at the laboratory temperature and air is passed, along with the slow oxidation of phosphorus, sulphur is oxidised to sulphurous and sulphuric acids. We have repeated some of these experiments and we have observed that a mixture of finely divided sulphur mixed with small bits of yellow phosphorus and kept under water at 25° or 30° can be oxidised to sulphurous and sulphuric acids and these can be qualitatively estimated.

Summary

A detailed experimental study has been made to ascertain whether phosphorus can be utilised as an inductor in the oxidation of carbonhydrate, fats and other substances and the following conclusions have been arrived at:—

(1) Finely divided phosphorus in the course of its oxidation has the greatest capacity of oxidising the carbohydrates and the fats, colloidal phosphorus comes second in order and small bits of phosphorus come last.

(2) In all the cases, the oxidation increases with time except in the case of colloidal phosphorus, where it does not vary much. This is due to the fact that the colloidal phosphorus prepared for this investigation is easily oxidised completely within six hours.

(3) The fumes of phosphorus and phosphorus trioxide also induce oxidation of the carbohydrates, fats and other substances to a slight extent.

(4) In the diffused light of the laboratory, carbohydrates, fats etc. are appreciably oxidised by air at the ordinary temperature.

(5) Although colloidal phosphorus should have been the most effective inductor, its apparent ineffectiveness is due to the presence of alcohol which inhibits the reaction.

(6) Under different conditions, amongst the carbohydrates, starch undergoes slow oxidation to the greatest extent.

(7) Sulphur is oxidised to sulphurous and sulphuric acid by simply bubbling air through a mixture of finely divided sulphur and phosphorus kept under water at the ordinary laboratory temperature.

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May 19, 1930.

THE SYSTEM $KCNS-Hg(CNS)_2-H_2O$

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The double thiocyanates of mercury have been known since 1838, when Claus[1] published his work on the metal thiocyanates. He prepared a double salt, by mixing $HgCl_2$ with KCNS and water, which he found to have the formula KCNS.2HgCNS.

Phillip[2] in 1867 stated that mercuric thiocyanate crystallized as needles and tablets, and also that when potassium thiocyanate is added to mercuric thiocyanate in warm water until the mercuric thiocyanate barely remains, a substance (no formula given) separates out. This substance is insoluble in cold water, slightly soluble in hot water, and it decomposes in cold water to give mercuric thiocyanate.

In 1872, Nordstroem[3] mentioned $Hg(CNS)_2.KCNS$ as colorless needles, and $Hg(CNS)_2.NH_4CNS$ as colorless prisms.

Fleischer[4] published his work on the double salts of NH_4CNS and Hg(CNS) in 1875. He prepared a double salt by adding yellow oxide of mercury to a boiling solution of NH_4CNS. He found the formula of this salt to be $2Hg(CNS)_2.N_2H_6.H_2O$. The crystals were in the orthorhombic system. Fleischer also prepared $Hg(CNS)_2.2NH_4CNS$ by dissolving $Hg(CNS)_2$ in an aqueous solution of NH_4CNS. By recrystallizing he obtained well-formed monoclinic crystals of this double salt. Drawings and crystal measurements of this double salt were made.

What is probably the most significant work on the double thiocyanates was performed by Rosenheim and Cohn[5] in 1901. They give three series of mercury double thiocyanates:

The monothiocyanates, HgCNSCl, HgCNSBr, and HgCNSOAc are described. Direct physical evidence of the complex cation HgCNS has not been obtained because of the slight solubility of these compounds.

The trithiocyanates, $KHg(CNS)_3$, $NH_4Hg(CNS)_3$, and $Ba[Hg(CNS)_3].2H_2O$ are well-crystallized salts, insoluble in cold water but easily soluble in hot water, by which they are decomposed into mercuric thiocyanate and the tetrathiocyanates.

Of the tetrathiocyanates, the potassium salt $K_2Hg(CNS)_4$ is obtained by crystallizing a mixture of the constituent salts. It crystallizes as colorless needles [?] and is easily soluble in water and alcohol. The sodium and barium salts are similar. The electrical conductivities of both the trithiocyanates and tetrathiocyanates show that they are salts of complex acids as do also their behaviors in Nernst's apparatus for demonstrating the movement of the ions.

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[1] Claus: J. prakt. Chem., **15**, 409 (1838).

[2] Phillip: Chem. Zentr., **55**, 967 (1867).

[3] Nordstroem: Bull. **17**, 345 (1872).

[4] Fleischer: Ann., **179**, 225 (1875); Bull. **26**, 165 (1876).

[5] Rosenheim and Cohn: Z. anorg. Chem., **27**, 280 (1901).

Sherrill and Skowronski[1] in 1905, showed by the results of freezing point, solubility, and E. M. F. determinations that the complex salt $K_2Hg(CNS)_4$ is formed in aqueous solution by the reaction of $Hg(CNS)_2$ and KCNS.

H. Grossman[2] in the same year stated that Hg^+ and Hg^{++} thiocyanates dissolve in KCNS to form the complex $K_2Hg(CNS)_4$. Measurements of concentration cells according to Bodländer's method showed that $K_2Hg(CNS)_4$ exists in solution, and in very dilute solutions some $KHg(CNS)_3$ also exists.

Potassium mercuric thiocyanate is of considerable importance as a reagent in microscopic qualitative analysis. Its use was first suggested by Chamot[3] as a substitute for the more deliquescent ammonium salt recommended by Behrens.

Experimental Part

A method of preparation of potassium mercuric thiocyanate is given by Chamot[4]: Freshly precipitated $Hg(CNS)_2$ is added to a cold 5% solution of KCNS, until a slight undissolved excess is present. The saturated solution is filtered and evaporated to crystallization.

The first phase to separate consists of many fine colorless needles, and on further concentration of the solution another type of crystal occurs as well formed monoclinic tablets. The latter phase continues to grow, and the needles dissolve, until eventually the solid phase consists entirely of the monoclinic tablets. The two phases are easily recognized microscopically as different from each other and from the simple mercury and potassium thiocyanates.

The above phenomena alone would seem to point to the fact that there are two double salts formed, but an additional clue is found in the behavior of the monoclinic tablets on dissolving

To the naked eye the tables appear to dissolve readily in cold water (Rosenheim and Cohn). If, however, the process of solution is followed under the microscope, another phase is seen to separate out in the neighborhood of the dissolving salt. This phase consists of small colorless needles or prismatic crystals, which in turn dissolve slowly in the solution.

When the needle-like crystals (from the first crop obtained in the above method of preparation) are placed in water they dissolve slowly, and another phase [$Hg(CNS)_2$] separates out in the vicinity. Strictly speaking, this is not a decomposition, although it has been stated in the literature on this double salt that the salt decomposes in water to form mercuric thiocyanate and the tetrathiocyanate (Rosenheim and Cohn: *loc. cit.*).

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[1] Sherrill and Skowronski: J. Am. Chem. Soc., **27**, 30 (1905).

[2] H. Grossman: Z. anorg. Chem., **43**, 356-369 (1905).

[3] "Elementary Chemical Microscopy," p. 353 (1921); Miss R. E. Chipman: Unpublished Thesis, Cornell University, 1917.

[4] Op. cit., p. 450.

The above behavior of the salts suggests that either double salt is capable of existing as a solid phase in the system at a given temperature. The decomposition of the double salts in water indicates that neither salt can be in equilibrium with a saturated solution of its own molecular composition. This is analogous to the behavior of the $KCl-CuCl_2-H_2O$ system and the $KCl-MgCl_2-H_2O$ (Carnallite) system.

The foregoing qualitative evidence points to the ternary system $KCNS-Hg(CNS)_2-H_2O$ being of the type of which the system $(NH_4)_2SO_4-NH_4NO_3-H_2O$ is the best known example.[1]

The present research was undertaken to obtain quantitative confirmation of these assumptions and to establish the chief points on the diagram at room temperature.

Preparation of Potassium Mercuric Thiocyanates

In order to study the effect of the concentrations of KCNS and $Hg(CNS)_2$ in determining the first phase to separate from the solution, and also in order to obtain some crystals of each double salt for analysis, solutions of different compositions were prepared and evaporated in a desiccator. The molecular ratios of $Hg(CNS)_2$ to KCNS were 1:1; 1:2; 1:5; and 1:10.

When equimolecular proportions of $Hg(CNS)_2$ and KCNS were dissolved in water (heating was necessary) and allowed to stand, the first phase to separate out consisted of platy crystals of $Hg(CNS)_2$. Then as the solution evaporated, needle-like crystals [$KHg(CNS)_3$] grew at the expense of the solid $Hg(CNS)_2$. When the solution had gone to dryness, a mass of yellowish needles was left. On recrystallization, the yellow color disappeared.

When the solution containing 2KCNS:1$Hg(CNS)_2$ was evaporated, the first phase to separate was the needle-like crystals [$KHg(CNS)_3$]. These gradually disappeared as the monoclinic tablets [$K_2Hg(CNS)_4$] formed and grew. The final product was a dense mass of poorly formed tabular crystals.

When the solutions of higher proportions of KCNS were allowed to evaporate, the tablets [$K_2Hg(CNS)_4$] were the first phase to separate out, and they were very well formed. Due to the extreme solubility of KCNS it is reasonable to expect that direct evidence of a change from the tablets to KCNS would be difficult to obtain, because in the KCNS range the solutions are very near dryness. Observation verified this.

The tablets or needles were removed from the mother liquor at various stages in the evaporations. They were washed in absolute alcohol because they are not very soluble in it, and therefore the solute in the alcoholic solution which displaces the watery mother liquor is very nearly of the composition of the salt being washed.

Analysis of Double Salts

To analyze either double salt, a known weight of the crystals was dissolved in warm water and a few drops of conc. HNO_3 were added to prevent hydrolysis. Some ferric ammonium alum was added, and the solution was titrated with $0.1N$ $Hg(NO_3)_2$ to the disappearance of the red color.[1]

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[1] The properties and the typical diagram of such systems are discussed by Clibbens: "Principles of the Phase Theory," pp. 86-92, 151-152 (1920).

The $Hg(NO_3)_2$ reacts with the KCNS in the mixture, but does not react with the $Hg(CNS)_2$. If KCNS alone is present, the reaction is:

$$2KCNS + Hg(NO_3)_2 \rightarrow \underline{Hg(CNS)_2} + 2KNO_3$$

If the KCNS is present as $K_2Hg(CNS)_4$, the reaction proceeds as follows:

$$K_2Hg(CNS)_4 + Hg(NO_3)_2 \rightarrow \underline{2Hg(CNS)_2} + 2KNO_3$$

and when KCNS is present as $KHg(CNS)_3$:

$$2KHg(CNS)_3 + Hg(NO_3)_2 \rightarrow \underline{3Hg(CNS)_2} + 2KNO_3$$

The mercury in the double salts was determined by precipitation as mercuric sulfide.[2]

The results of the analyses were as follows:

	Tablets		Needles
KCNS	39.4%		23.4%
	39.1		23.5
	39.0		
average	39.2	average	23.45
calculated for $K_2Hg(CNS)_4$-	38.0	calculated for $KHg(CNS)_3$-	23.42
Hg	38.8		48.8
	39.0		49.0
	39.1		
average	39.0	average	48.9
calculated for $K_2Hg(CNS)_4$-	39.2	calculated for $KHg(CNS)_3$-	48.4

A qualitative test for water showed that none was present in either the tablets or the needles. (This test entails heating the salt in a small glass tube which is sealed at one end. A short distance from the salt the inside of the tube is dusted with a water-soluble dye. If water is present in the salt, it is driven off and condenses on the dye and colors the tube. When the tablets were heated, even to decomposition, the test gave negative results.)

From these analyses it was concluded that the crystals having tabular form were the 2:1 double salt $K_2Hg(CNS)_4$, and that the needle-like or prismatic crystals were the 1:1 double salt $KHg(CNS)_3$.

Optical Properties of Double Salts

The needle-like crystals of the double salt $KHg(CNS)_3$ are apparently orthorhombic prisms 110, and pinacoids 100, terminated by domes 011. The terminal angle, between two dome faces, is about 158°.

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[1] Kolthoff and Furman: "Volumetric Analysis," p. 266 (1929).

[2] Treadwell and Hall: "Analytical Chemistry," Vol. II. p. 172 (1928).

All prismatic views exhibit parallel extinction, with very strong double refraction, and anomalous polarization colors which indicate that the double refraction is markedly greater for red than for violet. The axial plane is parallel to 100; the acute bisectrix is parallel to the elongation of the prisms, so interference figures are obtainable only from fragments. The material is biaxial, negative, with 2 V about 65-70°, $r < v$, marked. Optical orientation: $X = c$, $Y = b$, $Z = a$, $\text{Bx}_a = c$. Refractive indices: $\alpha = 1.735 \pm .005$; $\beta = 1.82$; $\gamma = 1.84$ (est).

The tabular crystals of the double salt $K_2Hg(CNS)_4$ are similar in habit to those of the ammonium double salt described by Koch.[1] They are short monoclinic prisms, with basal pinacoid, and when crystallized on a slide lie either on a pinacoid face 001 or a prism face 110. Hemipyramid and clinodome faces are occasionally developed.

As observed perpendicular to 001, the crystals are rhomb shaped in outline, with acute angles of about 80°. Some six- or eight-sided forms are formed, by the truncation of edges by the clinopinacoid 010 and the orthopinacoid 100. The basal view of the crystals shows symmetrical extinction with strong double refraction, the slower component vibrating parallel to the acute diagonal. Interference figures indicating that the "optical normal" is roughly parallel to the c axis are observable.

Crystals developed so as to lie on 110 are often markedly flattened, and have plane angles practically the same as those lying on 001, giving a rhomb shaped outline. One or more corners are often obliquely truncated by pyramid faces. This view of the crystals shows no sharp extinction, and its interference figures reveal an optic axis roughly perpendicular to the prism face.

Cliniopinacoidal views of the crystals are rare; they show an angle β of about 74°, and an extinction angle of about 22°. Interference figures are of the obtuse bisectrix type.

The material is biaxial, negative, with 2 V near 90°, and dispersion very strong, $r > v$. $\text{Bx}_o = b$. $\text{Bx}_a \wedge a = 22°$. Axial plane $\wedge$ 001 = 22°. Refractive indices: $\alpha = 1.645 \pm 005$; $\beta = 1.80$ (est); $\gamma = 1.9 +$ (est).

Establishment of the Ternary Diagram

As stated above, the microscopical behavior of these double salts when dissolving is direct evidence that the system $KCNS-Hg(CNS)_2-H_2O$ is of the type represented in the diagram shown in Fig. 1.

The most significant points on this diagram are:

A—The solubility of $Hg(CNS)_2$ in water

B—The composition of the invariant solution with which $Hg(CNS)_2$ and $KHg(CNS)_3$ can exist in equilibrium.

C—The composition of the invariant solution with which $KHg(CNS)_3$ and $K_2Hg(CNS)_4$ can exist in equilibrium.

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[1] Fleischer: Ann. **179**, 230 (1875).

D—The composition of the invariant solution with which $K_2Hg(CNS)_4$ and KCNS can exist in equilibrium.

E—The solubility of KCNS in water

F and G—The compositions of the two double salts.

The points *A* and *E* are known from the literature: Solubility of $Hg(CNS)_2$ at 25°—0.002 mols per liter, or 0.063% $Hg(CNS)_2$.[1] Solubility of KCNS at 25°—70.5 g. per 100 g. of solution, or 70.5%.[2]

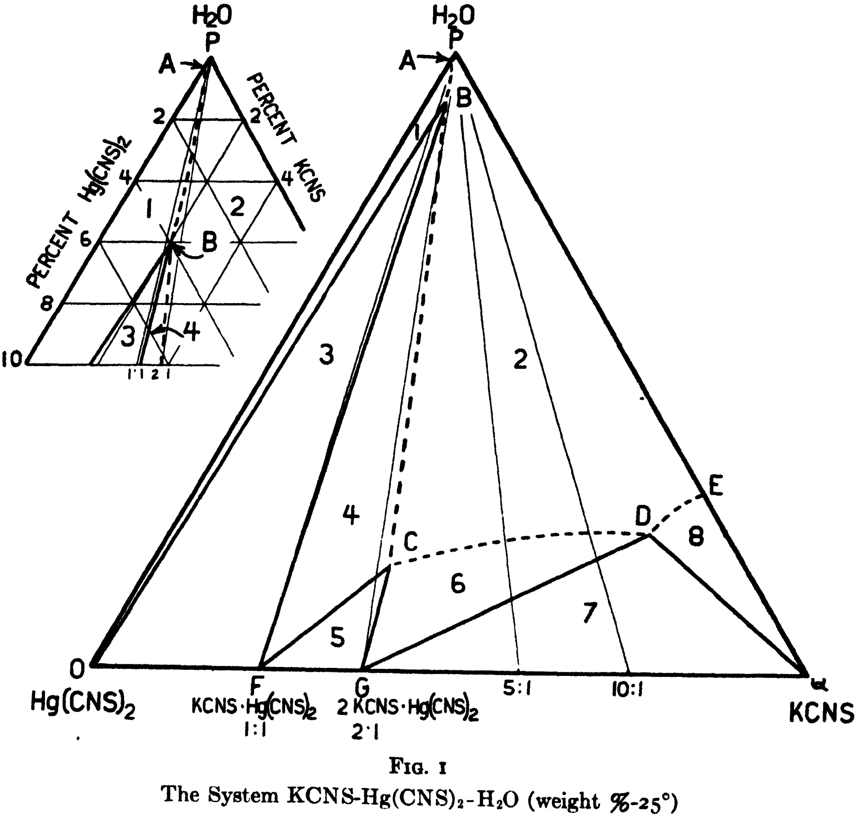

Fig. 1

The System KCNS-$Hg(CNS)_2$-H_2O (weight %-25°)

The points *F* and *G* might be determined by the method of indirect analysis using "tie lines,"[3] but since each of the double salts can be obtained in large well-formed crystals, and can be readily freed from the mother liquor, the analyses of these crystals suffice to furnish the required compositions.

The invariant points *B*, *C*, and *D* were determined by taking advantage of the fact that three phases of the system can coexist at these points. Microscopical examination enabled the identity of the two solid phases present to be established at any stage. This check on the observed constancy of composition of the solution at each invariant point was particularly useful, on account of the high solubility of KCNS and $K_2Hg(CNS)_4$, which rendered the establishment of equilibrium and subsequent sampling somewhat difficult.

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[1] Comey and Hahn: "Dictionary of Chemical Solubilities," p. 882 (1921).

[2] Seidell: "Dictionary of Solubilities," Vol. I, p. 566 (1919).

[3] Bancroft: J. Phys. Chem., 6, 178; Browne: 287 (1902).

If we add KCNS to a solution of $Hg(CNS)_2$ in contact with excess $Hg(CNS)_2$, the latter will be dissolved and the composition of the solution will vary along the curve *AB* until the invariant point *B* is reached. Here a second solid phase, $KHg(CNS)_3$, makes its appearance. Further addition of KCNS does not alter the composition of the solution, but does increase the amount of the double salt. The $KHg(CNS)_3$ is formed at the expense of the $Hg(CNS)_2$; until all the latter has been thus converted, the solution is saturated with respect to both solid phases and is of constant composition. There is thus a well defined invariant point, the coordinates of which may be determined by analysis of the solution when it becomes constant in composition. The actual solid phases present were also recognized microscopically.

For the point *B*, the composition of the solution is as follows:

	KCNS		$Hg(CNS)_2$		H_2O
	2.1		4.05		93.9
	2.1		3.9		94.0
	1.9		4.3		93.8
average	2.05%	average	4.05%	average	93.9%

Likewise, if still more KCNS is added after the point *B* is reached and all the $Hg(CNS)_2$ is used up, the composition of the solution will vary along the line *BC*. At *C* the second double salt $K_2Hg(CNS)_4$ will appear, the solution remaining constant in composition until all the $KHg(CNS)_3$ present has been converted to $K_2Hg(CNS)_4$. Both double salts coexist in contact with the solution, the composition *C* of which is as follows:

	KCNS		$Hg(CNS)_2$		H_2O
	33.1		49.4		17.8
	33.2		49.0		18.0
	33.0		48.9		17.6
average	33.1	average	49.1	average	17.8

In a similar manner the point *D* was established. The addition of KCNS to the solution containing an excess of solid $K_2Hg(CNS)_4$ will cause its composition to vary along the line *CD*. At the invariant point *D*, $K_2Hg(CNS)_4$ and KCNS coexist. The composition of the solution at *D* is as follows:

	KCNS		$Hg(CNS)_2$		H_2O
	66.8		10.8		23.6
	66.2		10.2		23.0
	66.2		10.2		23.0
average	66.4	average	10.4	average	23.2

The various areas represented in the accompanying diagram are:

(1) ABO = $Hg(CNS)_2$ and solution
(2) $ACDEP$ = solution
(3) OFB = $KHg(CNS)_3$, $Hg(CNS)_2$ and solution
(4) FCB = $KHg(CNS)_3$ and solution
(5) FGC = $KHg(CNS)_3$, $K_2Hg(CNS)_4$ and solution
(6) GDC = $K_2Hg(CNS)_4$ and solution
(7) GQD = $K_2Hg(CNS)_4$, KCNS and solution
(8) DQE = KCNS and solution

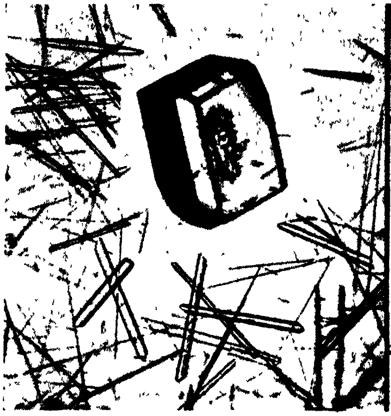

FIG. 2

Evaporation of a 2:1 molar system, within area 5. $K_2Hg(CNS)_4$ (tablet) growing; $KHg(CNS)_3$ (needles) dissolving. 100 ×.

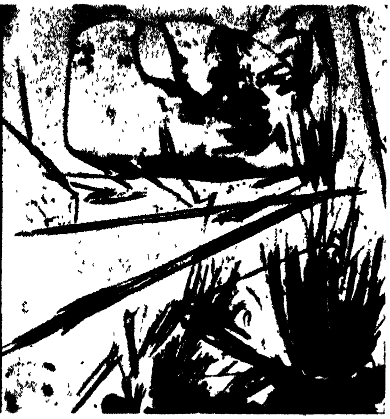

FIG. 3

Addition of water to the 2:1 salt, within area 5. $KHg(CNS)_3$ (needles) growing; $K_2Hg(CNS)_4$(tablets) dissolving. 50 ×.

The observed behavior, on evaporation, of solutions having various proportions of KCNS to $Hg(CNS)_2$, which has been briefly described above (page 1125) is indicated on the diagram along the lines radiating from P and intersecting OQ at the respective molecular ratios of 1:1, 2:1, 5:1, and 10:1.

For example, when the 2:1 solution is evaporated at room temperature, its concentration varies along the line PG until that line intersects BC. The 1:1 double salt $KHg(CNS)_3$, which is relatively slightly soluble in a solution of this composition, then begins to separate. As crystallization proceeds the composition of the mother liquor varies along the line BC, becoming relatively richer in KCNS until C is reached, at which point tablets of $K_2Hg(CNS)_4$ separate. (Fig. 2).

Crystallization of the 2:1 double salt from a solution of the composition represented by C would result in the solution becoming still richer in KCNS. However, any solution to the right of the line BC is not in equilibrium with the 1:1 salt, so the latter dissolves as evaporation continues. When the system has gone to dryness, at *G*, only $K_2Hg(CNS)_4$ will remain, provided supersaturation and imperfect diffusion have been avoided.

The observed behavior of the double salt $K_2Hg(CNS)_4$ on the addition of water is also in accordance with the diagram, as followed in the reverse direction along *GP*. Some $KHg(CNS)_3$ separates at once (in the area **5**), while $K_2Hg(CNS)_4$ dissolves, and as more water is added the needles of the former entirely replace the tablets of the latter (**6**). If sufficient water is added the needles finally dissolve completely (**2**). (See Figs. 4, 5, and 6).

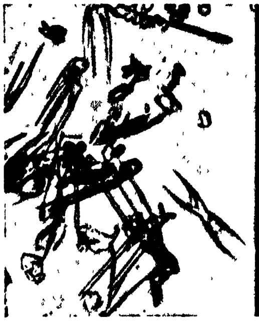
FIG. 4

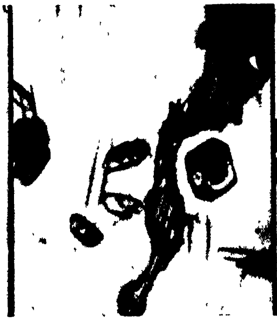
FIG. 5

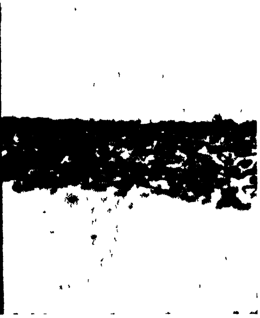
FIG. 6

FIG. 4. Evaporation of a 1:1 molar system, within area 3. $KHg(CNS)_3$(needles) growing; $Hg(CNS)_2$ (small grains) dissolving. 200 ×.

FIG. 5. Addition of water to the 1:1 salt, within area 3. $Hg(CNS)_2$ (tablets) growing; $KHg(CNS)_3$ (coarse needle) dissolving. 200 ×.

FIG. 6. $Hg(CNS)_2$ as a pseudomorph after addition of water to a needle of KHg $(CNS)_3$, in area 3. 100 ×.

In like manner the behavior of a solution containing 1:1 molecular proportions of KCNS and $Hg(CNS)_2$ may be correlated with the diagram. Crystals of $Hg(CNS)_2$ separate first, while the composition of the solution varies along *AB* to *B*. On further evaporation the double salt $KHg(CNS)_3$ grows at their expense, and is the only solid phase remaining when dryness is reached at *F*. When water is added to crystals of $KHg(CNS)_3$ they yield $Hg(CNS)_2$ (**3**), which remains after they have been dissolved (**1**), and on further dilution passes into solution (**2**). (See Figs. 4, 5, and 6).

The following table summarizes the behavior on evaporation of solutions having various molecular compositions.

Solution KCNS:$Hg(CNS)_2$	1st phase	2nd phase
1:1	$Hg(CNS)_2$	$KHg(CNS)_3$
2:1	$KHg(CNS)_3$	$K_2Hg(CNS)_4$
5:1	$K_2Hg(CNS)_4$	KCNS
10:1	$K_2Hg(CNS)_4$	KCNS

Solutions in the *DE* range on the diagram have a great tendency to supersaturate, and it was difficult to determine which phase actually tended to separate first under equilibrium conditions. In all other cases the microscopical observations were in agreement with the predictions from the diagram.

Since only the compositions and behavior of the double salts and the type of the system were sought, the solubility curves of the various solid phases (represented by dotted lines) were not determined experimentally, nor were observations made at other than room temperature (25°C).

The double salt $K_2Hg(CNS)_4$, which on account of its solubility is the one used as a reagent in microscopical qualitative analyses, can be made by either of two procedures:

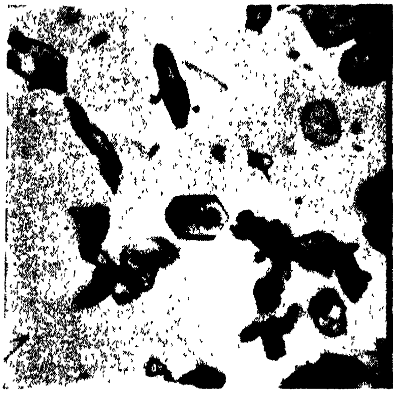

FIG. 7
$Hg(CNS)_2$ 200 ×.

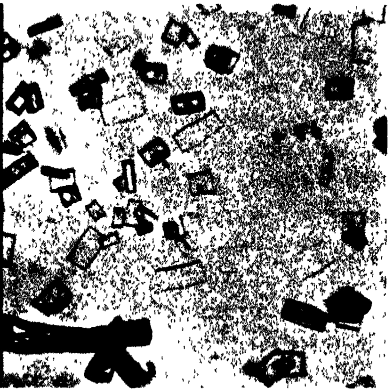

FIG. 8
KCNS 100 ×.

1. Dissolve a known amount of KCNS in water, add the equivalent amount of $Hg(CNS)_2$, and dilute until complete solution is obtained. Evaporate in a desiccator, stirring as dryness is approached.
2. Dissolve KCNS and $Hg(CNS)_2$ in water, in any ratio along the line *CD* (say preferably in molecular ratios between 2.5:1 and 5:1) and evaporate. Collect the first crops of tabular crystals, wash with alcohol, and dry.

Summary

1. At room temperature KCNS and $Hg(CNS)_2$ form two double salts—$KHg(CNS)_3$ and $K_2Hg(CNS)_4$, the optical properties of which are given.
2. Neither of these double salts is stable in contact with a saturated solution having the same molecular ratio of KCNS to $Hg(CNS)_2$ as the solid.
3. A ternary diagram summarizing the behavior of the system at 25° is given.
4. Methods are given for the preparation of $K_2Hg(CNS)_4$ for reagent use in microscopic qualitative analysis.

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CHEMICAL ACTIVITY AND PARTICLE SIZE

The Rate of Solution of Anhydrite below 70 Microns*

BY PAUL S. ROLLER**

Introduction

In connection with the work of this station on the problem of the utilization of anhydrite in the retardation of Portland cement, it was necessary to measure the rate of solution of anhydrite in water. This substance is generally known to be slowly soluble compared to the fully hydrated form of $CaSO_4$, gypsum, and apparently has a lower solubility. Inasmuch, however, as it is the unstable phase at room temperature[1] it was thought that its really greater solubility might become apparent if fine enough particles were used in the dissolution process. Accordingly the rate of solution of natural anhydrite in water was investigated quantitatively as a function of the particle size, and its saturation solubility determined with fine, rapidly dissolving grains.

Both equilibrium and kinetic effects on increasing the surface energy of a substance by decrease in the particle size have been noted. The thermodynamic consequences were derived in general form by Willard Gibbs[2] in 1876. Hulett[3] found that below 2 microns the solubility of gypsum began to increase and for particles 0.3 micron in size was 19 per cent higher than the normal value. The effects obtained with barium sulphate and mercuric oxide powders were considerably greater. Dundon and Mack[4] also obtained an increase in the solubility of gypsum between 0.2 and 0.5 micron in size, and Dundon extended these observations[5] to other powders, the maximum increase in solubility being 90 per cent. Tzentnershver and Knustinsons[6] found that the vapor pressure of various carbonates showed a decided increase for particles of the order of a micron.

On the kinetic side, no definite theoretical or quantitative experimental results are available on the effect of surface energy on the rate of a reaction. A number of interesting observations have been recorded, however, which indicate a much greater effect than that observed at equilibrium. Reboul[7] observed that the rate of attack on Ag, Cu, and Hg by a number of gases under reduced pressure was greater in proportion to the curvature. He worked with small planes, spheres, cylinders, and ellipsoids of the material.

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[1] van't Hoff et al.: Z. physik. Chem., **45**, 257-306 (1905).

[2] Gibbs: "Scientific Papers,".

[3] Hulett: Z. physik. Chem., **37**, 385 (1901); **47**, 357 (1904).

[4] Dundon and Mack: J. Am. Chem. Soc., **45**, 2479 (1923).

[5] Dundon: J. Am. Chem. Soc., **45**, 2658 (1923).

[6] Tzentnershver and Knustinsons: Z. physik. Chem., **132**, 185-8, (1928); **130**, 187-192 (1927).

[7] Reboul: Compt. rend., **155**, 1227 (1912); **156**; 549 (1913).

Sticks of NaOH, $NaNO_2$, etc., partly immersed in water and of Zn, Al, Mg. etc., in dilute acids were observed by Ganguly and Banerji[8] to be rapidly attacked at the air-solution-solid interface, while the remainder of the stick was uniformly and slowly dissolved.

Dehydrated and apparently insoluble Al_2O_3 and ZrO_2, when ground to 0-2.5 microns, were found by Podszus[9] to dissolve appreciably in HCl solution.

Recently, Luce[10] has, by an optical method, determined the attack on various solids by H_2S and halogen, and H_2SO_4 and HNO_3 solutions, and here again the reaction is most active in regions of great curvature.

On the basis of these observations, it was thought that the effect of decreasing particle size on the rate of solution of anhydrite might be considerable, though no noticeable effect on the saturation solubility would be expected since the smallest particle studied had a surface mean diameter of 2 microns.

Materials

A crystalline anhydrite from Midland, Calif., was used for the tests. It contained 0.2% water, less than 0.5% $CaCO_3$, no chlorides, and traces of iron and alumina.

Portions of the powder were fractioned into homogeneous particle size groups. The apparatus used was an air analyzer, to be described in a U. S. Bureau of Mines Technical Paper under the title "The Separation and Size Distribution of Microscopic Particles. An Air Analyzer for Fine Powders."

Microscopic analyses of the various fractions of the anhydrite powder, the diameter of a single particle being taken as the arithmetic mean of the length and breadth, are shown in Table I.

In Table I the distribution of the different sizes in each fraction is given on a weight per cent and a number per cent basis. Sundry particles below the lowest size limit shown here have been omitted; these aggregated in the worst case less than 0.5% by weight, averaging for all the fractions 0.2% by weight. In fraction II, there has been some overlapping with reference to fraction I, due to attrition by the air current of the fine grains during the separation.

Figs. 1-6 are microphotographs of the corresponding fractions in Table I. Figs. 1-4 are at 310 magnification (1 scale division = 3.3 microns); Figs. 5-6 at 70 magnification (1 scale division = 14.3 microns).

The mean diameter or each of the fractions may be defined in a number of ways. The arithmetic mean diameter is defined by the equation where

$$d_m = \Sigma d/n, \qquad (1)$$

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[8] Ganguly and Banerji: Z. anorg. allgem. Chem., **124**, 140-2 (1922).

[9] Podszus: Z. physik. Chem., **92**, 227-37 (1917).

[10] Luce: Ann. Physik., **11**, 167-251 (1929).

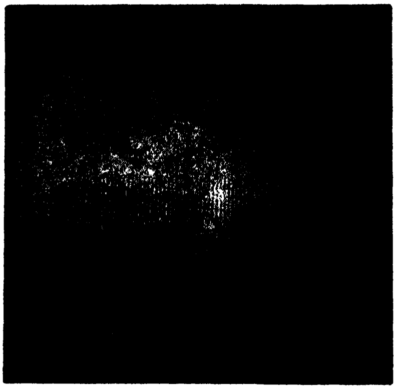

FIG. 1

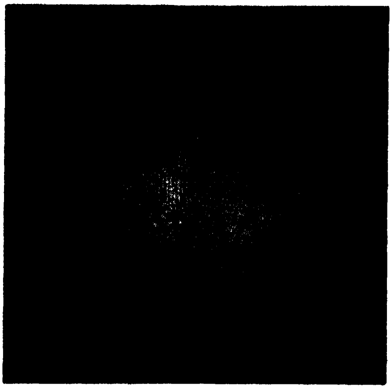

FIG. 2

FIG. 3

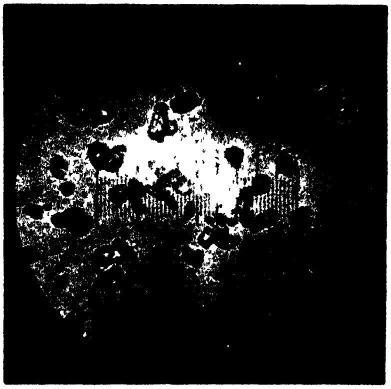

FIG. 4

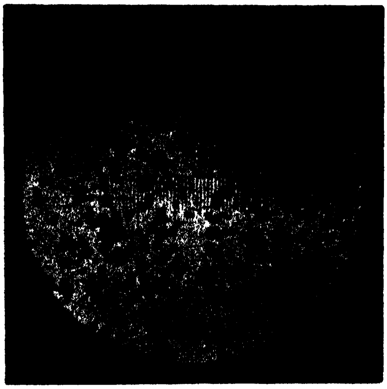

FIG. 5

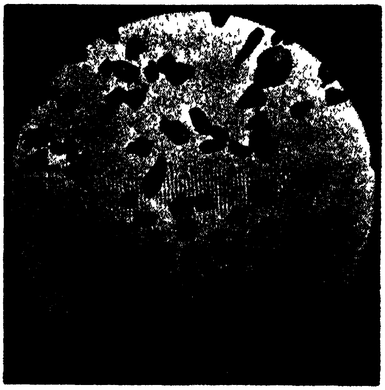

FIG. 6

TABLE I

Microscopic Analyses of Size Fractions of Anhydrite

Fraction No.								
	0-1	1-2	2-3	3-4				Microns
I	3.4	34.4	44.8	17.4				Weight per cent
	83.0	12.4	4.2	0.4				Number per cent
	0-1	1-2	2-3	3-4	4-5	5-6	6-7	Microns
II	2.3	13.3	31.2	7.9	23.5	21.2	11.3	Weight per cent
	66.0	23.5	7.3	0.9	1.5	0.6	0.2	Number per cent
	3-5	5-7	7-9	9-12				Microns
III	7.6	24.6	39.6	28.2				Weight per cent
	44.4	30.6	19.4	5.6				Number per cent
	7-10	10-15	15-20					Microns
IV	13.8	52.9	33.3					Weight per cent
	38.0	50.0	12.0					Number per cent
	12-15	15-20	20-25	25-35				Microns
V	2.4	13.7	38.0	45.9				Weight per cent
	12.0	24.0	42.0	22.0				Number per cent
	22-30	30-45	45-70	70-100				Microns
VI	0.2	3.5	40.4	55.9				Weight per cent
	6.1	12.2	51.0	30.7				Number per cent

the summation extends over each of the diameters of the n particles measured. However, the arithmetic mean has little weight as an indication of the properties of a powder, as it represents only the diameter of the particle which is numerically most frequent in the mixture of particle sizes.

It is more significant to define the mean diameter of a powder as the diameter of a hypothetical particle whose surface per unit weight is equal to the surface per unit weight of the powder. The quantity thus obtained may appropriately be called the surface mean diameter, d_s, and is defined by the equation

$$d_s = \Sigma d^3/\Sigma d^2 \qquad (2)$$

The surface mean diameter thus defined will be larger than the arithmetic mean in proportion to the range of particle sizes covered by the fraction.

The values of the surface mean diameter of each of the fractions of Table I, calculated by equation (2), are given in Table II. The arithmetic mean diameter calculated from equation (1) is shown in the last column of the table for comparison.

TABLE II

Arithmetic Mean and Surface Mean Diameter of Anhydrite Fractions

Fraction	Surface Mean Diameter (Microns)	Arithmetic Mean Diameter (Microns)
I	1.96	0.63
II	3.17	1.15
III	7.56	5.66
IV	14.1	12.4
V	25.8	23.2
VI	66.9	59.7

The results of Table II are accurate within 3 per cent. In fractions I and II, owing to the preponderance of the very smallest particles, the arithmetic mean is ½ to ⅓ the surface mean diameter. It is the latter, however, which is significant for the calculation connecting surface exposed to the rate of solution, and this is the diameter which will alone be referred to hereafter.

Method and Apparatus

The rates of solution were determined by means of a conductivity bridge. The water used in these experiments had a conductivity of 2×10^{-6} r.o. The conductivity electrodes were two parallel unprotected squares of platinized platinum led into narrow mercury-filled glass tubes which passed through a two-hole stopper. The electrodes and holders were rigidly fastened together. Both the water conductivity and the cell constant of the electrodes were frequently checked between experiments.

The solutions were contained in a tall glass beaker fitted with a hard rubber cover. Through a central hole passed a ⊥ -shaped stirrer made of hollow glass tubing and rotating at 470 r.p.m. The electrodes fitted tightly into a side-hole in the cover.

In making a run, 135 c.c. of water and a sample of the powder, usually 0.7 gram, were brought to temperature in a water bath at 20.00 ±0.03°C. With the stirrer rotating, the powder was rapidly thrown into the solution (by an assistant) and the initial time noted on a stop watch. Readings were thereafter taken at intervals. Curves were checked within 5 per cent by running a duplicate series, and the results averaged.

Specific conductivity readings were converted into concentrations, $CaSO_4$/100 c.c., by means of the empirical formula of Hulett:[11]

$$\frac{\text{mg mol}}{\text{liter}} = -.354 + 5211\ K_{25} + 841{,}400\ K_{25}^2.$$

In order to convert to 20°C., a percentage temperature coefficient, 0.21, was used, this being the average from Hulett's temperature-conductivity data. The resulting equation was:

$$\frac{\text{gr. } CaSO_4}{100 \text{ c.c.}} = -0.0048 + 78.37\ K_{20} + 13{,}970\ K_{20}^2. \tag{3}$$

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[11] Hulett: Z. physik. Chem., **42**, 581 (1903).

Results

In Table III is shown the concentration in solution against the time in minutes for each of the anhydrite size-fractions of Table II.

TABLE III

Time-Concentration Curves for Anhydrite Size-Fractions

Grams $CaSO_4$/100 c.c.

Min.	Surface		Mean		Diameter		
	1.96	3.17	7.56	14.1	25.8	66.9	Microns
0.15	.002	.003	.000	.004	.004	.002	
0.35	.0550	.0555	.0424	.0297	.0128	.0044	
0.60	.0882	.0911	.0812	.0411	.0168	.0074	
0.85	.1089	.1129	.0986	.0471	.0203	.0094	
1.35	.1352	.1391	.1134	.0555	.0257	.0128	
1.85	.1555	.1550	.1193	.0610	.0302	.0158	
2.85	.1782	.1758	.1278	.0677	.0367	.0198	
4.85	.1995	.1960	.1382	.0773	.0446	.0257	
6.85	.2096	.2059	.1431	.0818	.0486	.0292	
9.85	.2217	.2182	.1476	.0868	.0550	.0352	

The values given in Table III are plotted in Fig. 7. The results may be analyzed into three phases: There is an initial induction of about 0.1 minute. The concentration thereafter rises rapidly for a period, and then in the third phase, falls off to a slow continuous rate.

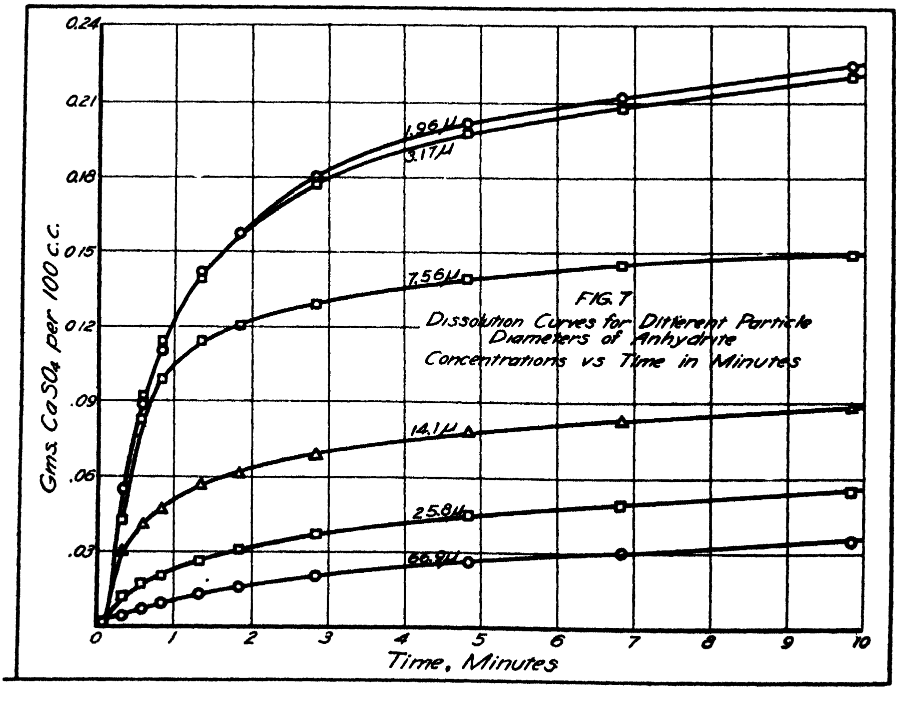
FIG. 7
Dissolution Curves for Different Particle Diameters of Anhydrite Concentrations vs Time in Minutes

The solubility of gypsum at 200°C. is 0.204 gram $CaSO_4$ per 100 c.c.[12] It is seen that at 7 minutes fractions I and II have already surpassed this solubility, the concentration still continuing to rise thereafter.

Rate of Solution vs. Particle Size:

No dissolution velocity constant, either monomolecular or bimolecular, could be calculated for any of the fractions. Owing to the induction period and other disturbances initially present, the relative rates of solution could not be determined by extrapolating the curves of Fig. 7 to zero time. It is necessary to base the determination of the relative rates upon the amount dissolved after a certain period. The procedure adopted for determining the relative velocity of solution of the different fractions was as follows: The fractions were considered in successive pairs, say III and IV. Considering fraction III, the dissolution curves were determined for multiples of the usual weight, 0.7 gram. These curves correspond to different surface exposures of fraction III. At a point 6 (or 3) minutes from the origin, on the slow portion of the dissolution curve, the corresponding ordinates were measured for each of the fractions IV and III, and for the different surface exposures of fraction III. On the assumption that the rate of solution is for a given fraction proportional to the surface exposure, a function connecting the concentration

TABLE IV

Comparison of Concentration Ordinates

Fraction	Surface Mean Diameter	Grams taken	Concentration Ordinate grams per 100 c.c. of solution	
			2.85 min.	5.85 min.
I	1 96	0 7		.2044
II	3 17	0.7		.2010
		1.4		.2434
III	7.56	7		.1401
		1.4		.1678
		2.8		.1960
IV	14.1	.7	.0679	0807
		2.8		.1228
		.35	.0436	
		.233	.0346	
V	25.8	.7	.0367	
		.35	.0222	
		.175	.0123	
VI	66.9	.7	.0198	

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[12] Böttger: Z. physik. Chem., **46**, 602 (1903).

ordinate with the rate of solution is obtained. By comparison and interpolation of the ordinates, the rate of solution of fraction IV with reference to III is obtained.

The relative specific surface of fraction III to fraction IV is in inverse ratio to the surface mean diameter. Correction was made for the surface reduction due to solution of the powder by subtracting from the initial surface the surface lost by solution up to the point of measurement, this procedure under the conditions being found most accurate. It is readily shown that for small losses the percentage reduction in surface is two-thirds the percentage reduction in weight.

In Table IV is given the results of the comparisons of the concentration ordinates at the end of 2.85 and 5.85 minutes for the different surface exposures of the different fractions.

From the results of Table IV, the ratio of the relative rate of solution against the relative specific surface for the fractions in pairs is obtained as indicated. By taking the relative specific surface and the relative rate of solution of the coarsest fraction equal to unity, the relative rate of solution per unit surface may be calculated for each particle size. For convenience the relative rate of solution per unit surface is called the dissolution factor. In Table V this quantity is calculated against the particle size.

TABLE V

Relative Rate of Solution of Different Particle Sizes of Anhydrite

Surface Mean Diameter	Relative Specific Surface	Relative Rate of Solution	Dissolution Factor
1.96	34.1	382	11.2
3.17	21.1	364	17.2
7.56	8.82	66.7	7.55
14.1	4.74	9.54	2.01
25.8	2.59	2.66	1.03
66.9	1.00	1.00	1.00

In Fig. 8 the results of Table V are plotted on semi-logarithmic paper as the dissolution factor against the surface mean particle diameter.

It is seen that down to a diameter of about 25 microns, the rate of solution per gram for different particles is proportional to the specific surface, and the dissolution factor is a constant, unity. This is the value to be expected if, as in the usual case, the rate of solution is proportional to the surface exposed. Below 25 microns, however, the rate increases more rapidly than the surface exposed up to 2.8 microns at which a maximum is reached. Here the rate of solution of the anhydrite is 17.6 times the proportional increase in surface. Below 2.8 microns the curve descends, but the dissolution factor is still as high as 11.6 at 1.96 microns.

The cause of the enhanced rate of solution of particle sizes of anhydrite below 25 microns, and the appearance of a maximum at 2.8 microns, is due probably to a number of concomitant effects. It is especially to be noted that the range of particle diameters for which the phenomenon occurs is less than the thickness of the diffusion film, 20-50 microns, calculated according to the theory of Noyes and Whitney[13], and Nernst[14], from the monomolecular dissolution rate of a plane surface in water.[15],[16] The initial induction period of about 0.1 second may actually correspond to the formation of a diffusion film of solute around the particle. The maximum at 2.8 microns is possibly due to the electrostatic charge which increases with decrease in particle size below about 20 microns. Further discussion of the cause and significance of these effects will be made in a later paper on the rate of solution of gypsum in its dependence on particle size.

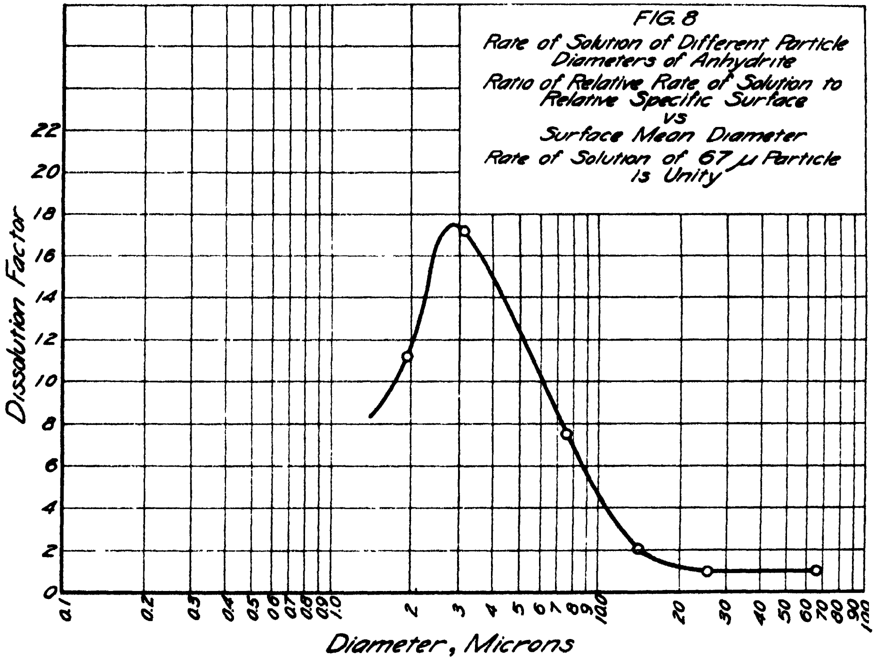

FIG. 8

Rate of Solution of Different Particle Diameters of Anhydrite

Ratio of Relative Rate of Solution to Relative Specific Surface vs Surface Mean Diameter

Rate of Solution of 67 μ Particle is Unity

Solubility of Anhydrite:

Anhydrite is the unstable phase of $CaSO_4$ at room temperature. In contact with water it changes into the stable phase, gypsum, but very slowly. The metastable solubility was determined at 20.0°C. by adding a quantity of finely divided powder to water, or to a saturated gypsum solution, and taking conductivity readings until these remained constant over a period of several hours. Thereafter the conductivity would fall, due to hydration of the anhydrite, to the value for gypsum.

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[13] Noyes and Whitney: Z. physik. Chem., **23**, 689 (1897).

[14] Nernst: Z. physik. Chem., **47**, 52 (1904).

[15] Brunner: Z. physik. Chem., **47**, 56 (1904).

[16] Wagner: Z. physik. Chem., **71**, 434 (1910).

1.4 grams of fraction II added to 135 c.c. of water at 20°C. showed a saturation conductivity of 2.602×10^{-3}r.o. 2.1 grams of fraction II in 135 c.c. saturated gypsum solution gave the value 2.600×10^{-3}r.o. 5 grams of a finely ground sample in 135 c.c. of gypsum solution supersaturated by 15% gave 2.622×10^{-3}r.o. The mean of these values is $2.608 \pm .006 \times 10^{-3}$r.o. To determine the concentration at this value we may extrapolate from the empirical equation of Hulett* reduced to 20°C. (equation (3)). Averaging the results, the value obtained for the saturation solubility of anhydrite is then 0.298 gr. $CaSO_4$/100 c.c. solution, or the solubility at 20°C. of natural anhydrite is 1.46 times that of gypsum.

Summary

1. A crystalline anhydrite was fractionated into six homogeneous size groups, ranging from a surface mean diameter of 1.96 microns to 66.9 microns.

2. The dissolution curves of these fractions were determined by conductivity measurements. There is an initial induction period of about .1 minute. In this as well as in general form the curves for the different particle sizes are similar.

3. For the finer particles, the rate of solution was not proportional to the surface exposed. The dissolution factor, i.e., the relative rate of solution per unit surface, is unity for particles above 25 microns. This is in accord with the well known law that the rate is proportional to surface exposed. Below this diameter, however, the dissolution factor increases to a maximum of 17.6 at 2.8 microns and then decreases. At a surface mean diameter of 1.96 microns the dissolution factor is 11.6.

4. The solubility of natural crystalline anhydrite in water was found to be 0.298 gr. $CaSO_4$/100 c.c. at 20°C.

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*Note: Dundon and Mack (Ref. 4) have by comparison shown that an extrapolation of the equation by over 300% is accurate to 1%.

THE OPTICAL ACTIVITY OF ELECTROLYTES

BY NEIL CAMPBELL

Introduction

The optical activity of electrolytes has been studied during the last fifty years in an attempt to throw light upon the nature of electrolytes in solution. The first investigator to provide accurate data was Landolt[1] who in 1873 carried out a detailed investigation on the normal salts of tartaric acid, and showed that they *all* had approximately the same value in 0.5 M solutions. Six years later Oudemans[2] investigated the different salts of the alkaloid quinamine, and found his results to be in harmony with those of Landolt. He accordingly formulated the generalisation known as Oudemans Law, which states that the different salts of an optically active acid or base have the same specific rotation in dilute solutions. Researches by Schneider,[3] Hartmann,[4] Darmois[5] have confirmed this law.

At this time there was no comprehensive theory concerning the nature of electrolytes in solution, and therefore the full significance of the Oudemans Law could not be appreciated. In 1887 however Arrhenius published his first paper on electrolytic dissociation and the value of the theory to account for the variation of the optical activity of electrolytes with change in concentration was soon recognised. In 1893 Hädrich[6] reviewed the work of Landolt and Oudemans in the light of the new theory and in addition determined the rotations of the salts of several optically active strong bases. As a result he extended the Oudemans Law. "The rotations of optically active electrolytes tend towards a definite value as the dilution is increased and this value is independent of the inactive ion." For example in very dilute solutions Hädrich showed that the different salts of the alkaloid quinidine had a molecular rotation of +726°. Hädrich showed that the ionisation theory gave a satisfactory and simple explanation of the Oudemans Law. On this theory changes of rotation of electrolytes with change in concentration are due to variations in the degree of dissociation: in sufficiently dilute solutions however the rotation depends solely on the presence of optically active ions since the degree of dissociation is practically complete.

A more accurate investigation of the Oudemans Law by Walden[7] using the metallic salts of the strong α-bromocamphor-π-sulphonic acid, showed

[1] Ber., **6**, 1073 (1873).
[2] Ann., **197**, 48 (1879).
[3] Ann., **207**, 257 (1880).
[4] Ber., **21**, 221 (1888).
[5] Ann. phys., **10**, 70 (1928).
[6] Z. physik. Chem., **12**, 476 (1893).
[7] Z. physik. Chem., **15**, 196 (1894).

that in very dilute solutions (1 gm. equivalent per 30 litres) the rotations of the several salts were *exactly* the same. Walden's results therefore served to confirm the correctness of the Oudemans Law, and in consequence were quoted as substantiating the Arrhenius theory. Walden however noted that at the dilution of 30 litres, conductivity measurements indicated that the salts were only 70%-90% dissociated. Noyes[1] pointed out that the rotations of these salts indicated 100% dissociation at the dilution considered; but, in view of the evidence to the contrary, he advanced a reason why this result should differ from that obtained from conductivity measurements. According to Noyes the optical activity of electrolytes depends essentially on the optical activity of ions, whether these ions be "free," or exist as "latent ions" in an undissociated molecule. Recently Walden[2] found that the molecular rotation of the tetra-ethyl-ammonium α-bromocamphor-π-sulphonate in a number of solvents is independent of the concentration at concentrations less than 1 gm. mol. per 17 litres. Walden maintains that there must be undissociated molecules present and explains the non-variation of the molecular rotation on lines similar to those of Noyes. Since Debye and Hückel advanced their theory based on the assumption that strong electrolytes are completely dissociated it is much easier to account for the fact that optical rotatory power measurements—and conductivity measurements—yield different values for the degree of dissociation of any given electrolyte. It is now established that the degree of ionisation of electrolytes is very much greater than that given by the conductivity ratio Λ_c/Λ_∞ and in dilute solutions such as those considered by Walden (1/30 M) the degree of dissociation is probably practically complete. (It is of interest to note that the optical activity measurements of Walden gave the first indication that the degree of ionisation as calculated from conductivity data was incorrect). When moderately concentrated solutions are examined however, it is found that the different salts possess different rotations (e.g. the metallic tartrates); such differences may be explained by assuming the presence of undissociated molecules. (Hädrich). Thus while the optical activity of electrolytes in dilute solutions substantiates the complete ionisation theory, the Arrhenius theory offers a simple explanation of the variations observed at greater concentrations. As a result the optical rotatory power of electrolytes has been quoted both as evidence for the Arrhenius theory and as evidence for the Debye-Hückel theory. (For a discussion on this point a recent paper by Jacobs and King[3] may be consulted).

In view of the uncertain knowledge regarding the nature of electrolytic solutions it is of interest to study further the optical rotation of electrolytes in solution. It is the purpose of this communication to investigate the changes in rotation of the electrolyte ammonium α-bromocamphor-π-sulphonate caused by (1) change of concentration (2) addition of optically inactive electrolytes and non-electrolytes (3) change of solvent.

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[1] Science, **20**, 577 (1904).

[2] Monatshefte, **53-54**, 14 (1929).

[3] J. Phys. Chem., **34**, 1013 (1930).

It may be mentioned at this point that the majority of optically active electrolytes hitherto examined have been hydroxy derivatives of succinic acid, although it has long been recognized that these compounds possess peculiar properties, due to the presence of polar groups. (This point has been stressed in a recent paper by Bancroft[1]). Moreover a number of investigators have examined optically active acids. That their conclusions must be accepted with reserve is obvious since the hydrogen ion is unique in that it has both donor and acceptor properties. It therefore appears unfortunate that so many of the optically active electrolytes examined possess properties not characteristic of electrolytes in general. It must be admitted on the other hand that the alternatives—usually members of the camphor series or alkaloid bases—are open to objection on account of their complex structure. In the present research ammonium α-bromocamphor-π-sulphonate was chosen not only because it is a typical strong electrolyte, but also because it does not possess any group such as the amino or hydroxyl. The present paper deals mainly with the variations in the rotation of this electrolyte.

Experimental

In carrying out this research nearly all the solutions examined contained the same concentration of the active ammonium salt—molecular concentration 0.1. In order that the rotations might be strictly comparable it was necessary that there should always be the same quantity of ammonium salt between the end plates of the polarimeter tube. Careful attention was therefore given to the weights, volumes, and temperatures of the solutions.

The weight of water in each solution was determined from density measurements.

All volume and density measurements were determined at 20°C. The mercury green line was used in all the polarimetric observations.

Apparatus. The polarimeter was a Hilger instrument provided with a Lippich three-shadow polariser and two verniers reading to 0.01°. It was fitted with a direct-vision spectroscope attachment for reading rotations with the mercury green line. The tube was 4 dcm. in length and was provided with a water jacket through which water was pumped from a thermostat by means of an electrically driven water turbine. The temperature of the water in the thermostat was so regulated that the solution in the polarimeter tube was maintained at 20.0°C. ($\pm$0.20).

A quartz mercury vapour lamp working at atmospheric pressure was used as a source of light for the mercury green line.

The standard flasks were all calibrated.

The pyknometers were of the usual Ostwald type, with a capacity of about 5 c.c. All densities were referred to water at 20.0°C.

Chemicals. The chemicals were for the most part Analytical Reagents. Each reagent was tested for gross impurities by the standard methods and were purified where necessary. In cases of doubt the reagents were analysed.

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[1] J. Phys. Chem., **34**, 897 (1930).

The ammonium α-bromocamphor-π-sulphonate was obtained from the British Drug Houses, Ltd., and was recrystallised from hot water and dried in vacuo over sulphuric acid. The pure salt had a rotation $[M]^{20}_{5461} = +347.2°$: molar conc. of solution = 0.1; cf. the figures of Pope and Read:[1] $]M]^{20}_{5461} = + 346.6°$; molar conc. = 0.2 (approx.).

Accuracy of the Results. Repeated experiments showed that the readings were accurate to 0.02° except in the case of a few solutions such as those containing methyl alcohol. As most of the angles measured were approximately +13° an accuracy of 1 in 500 may legitimately be claimed. Little difficulty was experienced in obtaining weight and volume measurements with this degree of accuracy.

Data and Discussion

Variation of the Molecular Rotation of electrolytes with change of concentration.

In the case of ammonium-α-bromocamphor-π-sulphonate a small but definite increase in the molecular rotation with increase in the concentration was observed.

TABLE I

Molar conc. Amm. Salt	$[M]^{20}_{5461}$	Molar Conc. Amm. Salt	$[M]^{20}_{5461}$
0.02	+345°	0.20	+349.6°
0.04	+345°	0.30	+353.5°
0.10	+347.2°		

These changes are very similar to those observed by Darmois[2] in the case of several tartrates. It appears that below molar concentrations of 0.1 there is little or no variation in the molecular rotations of such salts. This is in agreement with Walden's values for the tetra-ethyl ammonium salt of α-bromo-camphor-π-sulphonic acid—$C_{10}H_{14}BrOSO_3^- + N(Et)_4^+$—in aqueous solution and with the figures quoted by him for several tartrates. It therefore appears that in many cases solutions whose concentrations are less than 0.1 M exhibit no change in rotation with dilution.

A statement by G. N. Lewis[3] on the additive properties of electrolytic solutions may be commented on at this point. "Indeed in all strong electrolytes the partial volume, heat capacity, internal energy, viscosity, refractive index, rotatory power—in fact practically all the significant physical properties of the undissociated part of the electrolyte—seem practically identical with the properties of the constituent ions. If we had no other criterion for the degree of dissociation, these facts would undoubtedly lead one to regard salts up to a concentration of normal or half normal as completely dissociated." So far as results from the study of the optical activity of electrolytes furnish information as to the dissociation of electrolytes this statement by Lewis does not hold for solutions whose concentrations are greater than 0.1M.

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[1] J. Chem. Soc., 97, 2201 (1910).

[2] Loc. cit.

[3] Z. physik. Chem., 70, 214 (1910).

The changes in rotation at higher concentrations may be adequately explained by change in the degree of dissociation of the electrolyte. Recently however Darmois[1] assuming complete dissociation even in concentrated solutions has advanced another theory based on the ionic deformation theory of Fajans. Darmois studied the variation of the rotations of several tartrates and accounts for these changes by the "deformation effect" of the charged cations on the tartrate ions. The work of Fajans[2] shows that in general it is the anions which undergo deformation under the influence of the more compact cations and further that the deformation produced depends on the radius and charge of the cation. Darmois showed that the influence of the cations on the optically active tartrate ions was inversely proportional to the ionic radii as is to be expected from Fajans theory. The deformation theory is not sufficient to account for all the changes in the rotatory power observed and Darmois assumed in addition a "dehydration" process. Stubbs[3] and Patterson and Anderson[4] on the other hand found evidence against such an assumption. Darmois' theory however explains the variations in the rotatory power satisfactorily.

Summarising it may be stated that there are two theories accounting for the variation of the optical rotation of electrolytes with change of concentration. At present there is not enough evidence to enable one to decide which theory is to be preferred.

It is of interest to enquire whether there is any simple relationship between the changes of the optical activity of an electrolyte and the changes in the thermodynamic activity of the electrolyte or its ions. In the present state of our knowledge it is impossible to discuss this matter fully, since the changes in the activity coefficients of ions with concentration cannot be determined except by making certain arbitrary assumptions which may or may not be justified. The activities of electrolytes in aqueous solution have been accurately determined. When the activity coefficients of an electrolyte are plotted against its molecular concentration a characteristic curve is obtained: the curve falling to a minimum and then rising steeply. The nature of the curves obtained by plotting the molecular rotation of an electrolyte against the molar concentration varies. In some cases they assume the form of straight lines and in no case do they give rise to a maximum or minimum, so that there is no obvious correlation between the changes in the optical rotation of an electrolyte and its thermodynamic activity.

Effect on the Molecular Rotation of Electrolytes produced by the Addition of Optically Inactive Electrolytes and Non-Electrolytes.

The effect of adding a fixed weight of potassium chloride to solutions of the ammonium salt was first investigated.

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[1] Loc. cit.; Trans. Faraday Soc., **26**, 384 (1930).

[2] Trans. Faraday Soc., **23**, 357 (1927), etc.

[3] J. Chem. Soc., **99**, 2265 (1911).

[4] J. Chem. Soc., **101**, 1833 (1912).

Rotations of Ammonium Salt in presence of Potassium Chloride.

Molar concentration of KCl = 1.0.

Δ = Increase in the molecular rotation of the ammonium salt in a solution containing KCl 1.0 M, and the molecular rotation in aqueous solution.

Molar Conc. Amm. Salt	$[M]^{20}_{5461}$	Δ	Molar Conc. Amm. Salt	$[M]^{20}_{5461}$	Δ
0.02	+347.9°	2.9°	0.20	353.4°	3.8°
0.04	348.7°	3.7°	0.30	357.5°	3.7°
0.10	349.8°	3.7°			

It is evident that the increase in the molecular rotation of the ammonium salt caused by the addition of a definite weight of potassium chloride is independent of the concentration of the ammonium salt. This is in harmony with the conclusions of Stubbs[1] in regard to the effect of adding salts to l-malic acid "that the influence of the salt on the specific rotation depends mainly on the concentration of the solution with regard to that salt, and not on the concentration of the malic acid present."

An extensive investigation into the influence of different types of electrolytes and non-electrolytes on the rotations of 0.1M solutions of ammonium α-bromocamphor-π-sulphonate was made.

If Damois' view is correct it is to be expected that the addition of inorganic salts to the salt of an optically active acid will result in changes of the molecular rotation of the electrolyte: and further that the following regularities will be observed. The magnitude of the change of rotation will be (1) inversely proportional to the size of the added cation: (2) proportional to the charge of the added cation: (3) dependent on the concentration of the added salt. The effect of adding inorganic salts to optically active electrolytes has been investigated by many workers among whom may be mentioned Stubbs[2], Patterson and Anderson[3], Darmois[4] and Mrs. Liquier-Milward.[5] All these authors succeeded in obtaining interesting regularities. In order to investigate the matter further, many salts of different types were added to solutions of ammonium-α-bromocamphor-π-sulphonate. In addition the effects of acids of different strengths, and non-electrolytes such as alcohol were observed. The changes in rotation produced in this way may be seen in the following table.

Amm. α-bromocamphor-π-sulphonate. Molar Conc. 0.1. Effect on the rotation produced by the addition of various salts, etc.

The molar concentration of the added substance in all cases was 0.5.

Δ = Increase in $[M]^{20}_{5461}$ caused by addition of inactive compound. The probable experimental error ± 0.6°.

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[1] Loc. cit.

[2] Loc. cit.

[3] Loc. cit.

[4] Loc. cit.

[5] Trans. Faraday Soc., 26, 390 (1930).

TABLE II

Added Compound	Δ	Added Compound	Δ
$CH_3.COOH$	0.0°	$CdSO_4$	2.2°
HCl	0.3°	NaI	2.7°
CH_3OH	0.3°	Na_2SO_4	2.9°
NH_4Cl	0.4°	$(NH_4)_2SO_4$	3.1°
$BaCl_2$	0.4°	$CH_2Cl.COOH$	3.4°
LiCl	0.9°	KI	3.4°
Urea	0.9°	$MgSO_4$	3.4°
$CdCl_2$	1.1°	K_2SO_4	4.2°
NaCl	1.4°	K_2CrO_4	4.2°
KBr	1.4°	$CHCl_2.COOH$	5.2°
Glycerol	1.7°	$CCl_3.COOH$	5.2°
KF	2.0°	CdI_2	10.0°
KCl	2.0°	$K_4Fe(CN)_6$	12.0°

Table II serves to show that:—

(1) The change produced by the addition of these substances is small compared with those observed by Darmois and the other workers in this field. For example Darmois found that the specific rotation of a 0.25 M solution of sodium tartrate decreased from + 42.5 to +23.0° in the presence of $BaCl_2$ (0.6M). The greatest change observed in the case of the ammonium α-bromocamphor-π-sulphonate is in the case of potassium ferrocyanide, i.e. the molecular rotation increased from +347.2° to 359.2°.

(2) The magnitude of the change of rotation cannot be correlated with the charges or size of the ions. This is shown more clearly by Tables III and IV.

TABLE III

Molar Conc. of salt = 0.5	Δ
HCl	0.3°
NH_4Cl	0.4°
$BaCl_2$	0.4°
LiCl	0 9°
$CdCl_2$	1.1°
NaCl	1.4°
KCl	2.0°

TABLE IV

Molar Conc. of salt = 0.5	Δ
KBr	1.4°
KF	2.0°
KCl	2.0°
KI	3.4°
K_2SO_4	4.2°
$K_2C_2O_4$	4.2°

Indeed it is obvious that the effect cannot be purely ionic since weak electrolytes such as monochloracetic acid and non-electrolytes like glycerol have greater effects on the rotation than most of the salts mentioned above. It is manifest therefore that in the case of ammonium α-bromocamphor-π-sulphonate no regularities are obtained such as those observed by Darmois in the normal tartrates.

Since according to the modern views the properties of solutions of electrolytes are determined to a large extent by the value of $\sqrt{\Gamma}$ where $\Gamma =$ twice the ionic strength, the molecular rotation of the ammonium salt was plotted against $\sqrt{\Gamma}$. This has already been done by Mrs. J. Liquier-Milward[1] in her study of the effect of neutral salts on the rotation of asparagine, who found from her curves that the salt effect depended on the degree of ionisation of the salt added. Thus salts such as NaCl had the greatest effect, while weakly ionised salts like $CdCl_2$ had the least influence. Salts of the type of $MgSO_4.K_2SO_4$, had intermediate values. The results obtained in the present research are shown in Table V and Fig. 1.

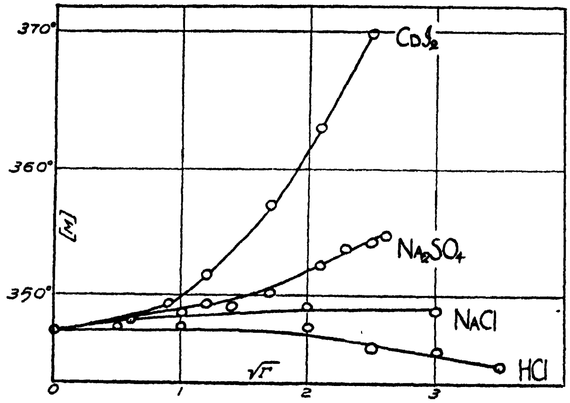

Fig. 1

TABLE V

Conc. of Amm. salt = 0.1M μ = ionic strength $\Gamma = 2\mu$

HCl Molar Conc.	$\sqrt{\Gamma}$	[M]	NaCl Molar Conc.	$\sqrt{\Gamma}$	[M]
—	—	+347.2°			
0.5	1.0	+347.5°	0.2	0.6	+347.6°
1.0	1.4	+347.5°	0.5	1.0	+348.6°
2.0	2.0	+347.5°	1.0	1.4	+349.2°
2.5	2.2	+345.9°	2.0	2.0	+349.2°
3.0	2.5	+345.7°	3.0	2.5	+348.9°
3.5	2.7	+344.2°			
Na_2SO_4	$\sqrt{\Gamma}$		CdI_2	$\sqrt{\Gamma}$	
0.25	1.2	+349.4°	0.125	0.9	+348.9°
0.5	1.7	+350.1°	0.25	1.2	+351.6°
0.75	2.1	+352.4°	0.5	1.7	+357.2°
0.875	2.3	+353.6°	0.75	2.1	+362.9°
1.0	2.5	+354.1°	1.0	2.5	+369.9°
1.125	2.6	+354.6°			

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[1] Loc. cit.

It is clear that the regularities obtained by Mrs. Liquier-Milward have not been obtained in the present instance. Whereas this investigator found that the effect of neutral salts on the rotation of an electrolyte was directly proportional to the degree of ionisation of the salts exactly the reverse is shown by the above figures.

$$CdI_2 > Na_2SO_4 > NaCl.$$

The alternative explanation is that the above changes in rotation are due to repression of the ionisation of the optically active electrolyte caused by the addition of the inorganic salts. It is not easy to test this theory quantitatively since the laws governing the equilibrium of electrolytes are not thoroughly understood. The equilibrium expressions which have been obtained are derived from the isohydric principle which in turn is based on the law of mass action. As strong electrolytes do not obey this law, such expressions are largely of an empiric nature and must be used with caution. It is unlikely however that decrease in the degree of ionisation is the important factor since, as has already been shown, neutral substances like urea influence the rotation to the same extent as many of the salts while weak electrolytes like cadmium iodide and monochloracetic acid have a greater effect.

The above method of treating solutions is open to criticism and indeed the possibility of examining quantitatively equilibria between ions and undissociated molecules has been questioned.[1] Moreover the determination of the ionic concentrations present in solution is attended by great difficulties since the degree of dissociation of electrolytes is not known with certainty. In view of such difficulties the problem of electrolytic solutions has been attacked from the thermodynamic standpoint. The thermodynamic method has proved very fruitful and it is of interest to review the results of the present research from this point of view. From the fact that the thermodynamic activities of salts are conditioned by the type of electrolyte, some relationship might be expected to exist between the salt type and the effect on the optical rotatory power of an electrolyte. As shown in Table VI, however, salts of different types have practically the same effect on the rotation of the optically active salt.

TABLE VI

Molality = 0.1.

Salt	Active Coefficient	△
KCl	0.794	2.0°
$BaCl_2$	0.501	0.4°
$MgSO_4$	0.166	1.1°

The thermodynamic activities of the salts and their effects on the optical activity of ammonium α-bromocamphor-π-sulphonate do not seem to be related. This is hardly surprising as the effect may depend essentially on the activities of the positive ions. As already mentioned the activities of ions cannot be determined with certainty and therefore no conclusions can be drawn as to whether or not the thermodynamic activity of an ion and its effect on the optical activity of an electrolyte are related.

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[1] Lewis and Randall: "Thermodynamics," p. 323.

The effect of adding excess of optically inactive substances was investigated and the results are shown in Table VII and Fig. 2.

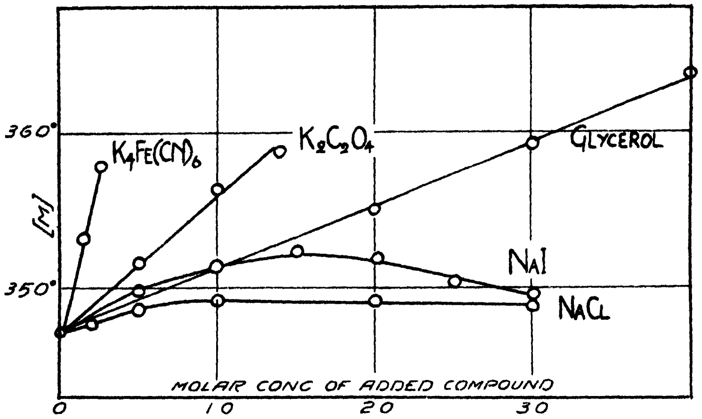

FIG. 2

TABLE VII

Sodium Chloride

Molar Conc.	[M]
—	+347.2°
0.5	+348.6°
1.0	+349.2°
2.0	+349.2°
3.0	+348.9°

Potassium Oxalate

Molar Conc.	[M]
0.25	+350.1°
0.5	+351.6°
1.0	+356.3°
1.375	+358.8°

Sodium Iodide

0.5	+349.9°
1.0	+351.4°
1.5	+352.4°
2.0	+351.8°
3.0	+349.7°

Potassium Ferrocyanide

0.125	+351.1°
0.25	+353.1°

Glycerol

0.5	+348.9°
1.0	+351.1°
2.0	+355.1°
3.0	+359.3°
4.0	+363.9°

For the sake of clarity only the curves of a few salts are given. These are representative and typical. Thus uni-univalent salts give curves similar to that of sodium chloride or sodium iodide while uni-divalent salts have an influence very like potassium oxalate.

The difficulties attending a correlation between the variation of rotation and the known properties of the added compounds are apparent. This is further emphasised by a consideration of Tables VIII and Fig. 3, where the effect of acids and non-electrolytes is shown.

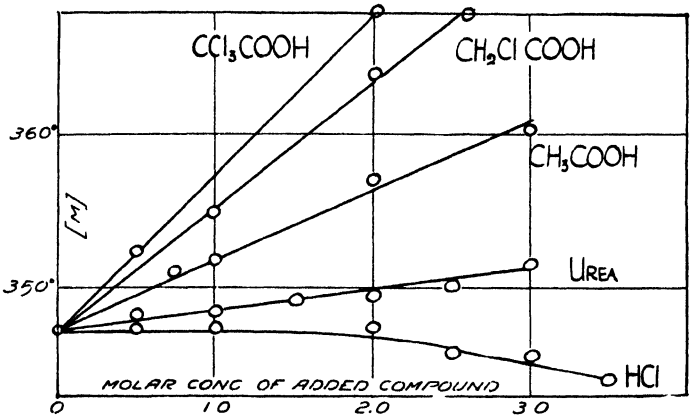

FIG. 3

TABLE VIII

Hydrochloric acid		Acetic acid	
Molar Conc.	[M]	Molar Conc.	[M]
—	+347·2°	—	+347·2°
0·5	+347·5°	0·5	+347·2°
1.0	+347·5°	0·75	+351·1°
2.0	+347·5°	1.0	+351 9°
2·5	+345·9°	2.0	+357·2°
3·0	+345·7°	3·0	+360.5°
Monochloracetic acid		Dichloracetic acid	
—	+346.9°	—	+347·2°
1.0	+354·6°	0.27	+349·4°
2.0	+363·9°	0·53	+352.6°
2.7	+368.6°		
Trichloracetic acid		Urea	
—	+346.9°	—	+347·2°
0·335	+349·7°	0·5	+348.1°
0·5	+352·4°	1.0	+348·3°
2.28	+383·3°	1·5	+349·2°
2·5	+386.4°	2.0	+349·4°
		2·5	+350·3°
		3·0	+351.6°

Two conclusions may be drawn from a study of the above graphs namely, that the influence of electrolytes on the rotation of ammonium α-bromocamphor-π-sulphonic acid is small, and that the effect is not conditioned solely by the ionic nature of the added substance. The theory that the variations of rotation are due essentially to the direct influence of cations on the optically active ion must therefore be considered as incomplete. This is only to be expected in view of the scanty nature of our knowledge of solutions. In considering the optical rotatory power of electrolytes in solution, no account has been taken of the polar nature of the solvent (in most cases water) which results in the solvent dipoles being attracted to the solute molecules or ions. This interaction between solvent and solute molecules may be expected to influence the rotation of the optically active ions and consequently must be taken into account in any discussion on the optical rotatory power of electrolytes. At present the nature of this effect is not fully understood. Further the dielectric constant of the solvent must be taken into consideration. In order to examine the rotations of an electrolyte in solutions of different dielectric constants, aqueous alcohol solutions of ammonium α-bromocamphor-π-sulphonate were investigated.

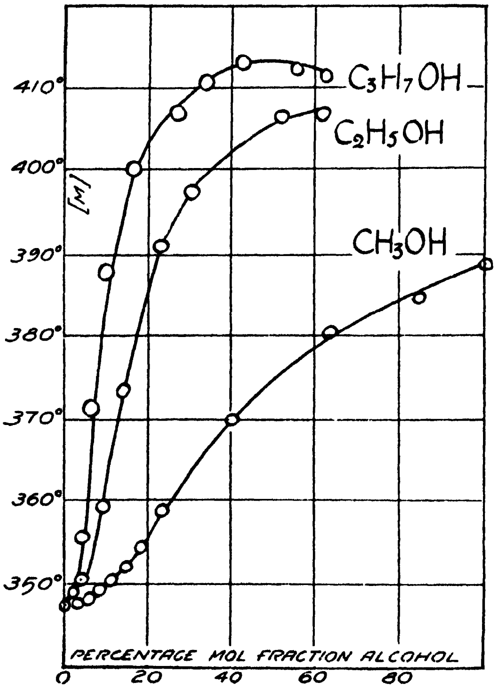

FIG. 4

When the molecular rotation of the ammonium salt is plotted against the mol. fraction of alcohol S-shaped curves are obtained in all cases (Fig. 4). It certainly appears that lowering the dielectric constant of the solvent is accompanied by an increase in the rotation, but the nature of the curves indicates that some other effect or effects must be considered. It would be rash to suggest what these effects are, until more data are provided regarding the optical activity of salts in mixed solvents.

TABLE IX

A = Percentage Mol Fraction Alcohol

A	[M]	A	[M]
	Methyl Alcohol		
—	+347.2°	14.9	+352.2°
0.9	+347.2°	17.5	+354.6°
1.9	+347.2°	23.0	+359.0°
3.8	+347.6°	39.8	+369.9°
5.9	+348.1°	63.2	+380.3°
8.0	+349.4°	84.9	+384.8°
10.2	+349.4°	100.0	+389.0
11.4	+350.3°		
	Ethyl Alcohol		
—	+347.2°	22.8	+391.1°
1.9	+348.1°	29.6	+397.4°
3.9	+350.6°	51.2	+406.8°
8.6	+359.6°	60.6	+406.8°
14.1	+373.5°		
	Propyl Alcohol		
—	+347.2°	26.5	+407.1°
0.9	+348.1°	33.4	+410.9°
1.9	+350.0°	42.3	+413.0°
7.0	+371.4°	57.5	+412.4°
9.3	+387.9°	60.2	+411.8°
16.4	+401.2°		

Summary

1. The work done on the rotatory power of optically active electrolytes is reviewed, and the merits of the theories advanced to account for the variations of the rotations of electrolytes are considered.

2. The rotations of ammonium α-bromocamphor-π-sulphonate have been studied.

In aqueous solutions below molar concentrations of 0.1 there is little or no variation in the value of the molecular rotation. This is in agreement with the results of other investigators on the tartrates, etc. The changes observed at greater concentrations may be adequately explained either by variation in the degree of ionisation, or by Darmois' deformation theory.

The effect of adding optically inactive salts and non-electrolytes has been investigated. The regularities observed by other authors have not been observed. Non-electrolytes have a decided influence.

3. The optical rotatory power of the ammonium salt in aqueous alcohol solutions has been examined.

In conclusion the author has much pleasure in thanking Sir James Walker for his valuable advice and guidance throughout the research.

Edinburgh University,
October 1, 1930.

QUANTITATIVE X-RAY ANALYSIS

Copper-Silver and Copper-Zinc Alloys

BY HENRY TERREY AND ERIC GEORGE VICTORY BARRETT

Introduction

The application of X-ray spectroscopy to chemical analysis may be said to have commenced with the work of Moseley[1] on the relationship between the atomic number of an element and the frequency of its characteristic radiation. In the realm of qualitative analysis, X-ray spectroscopy has demonstrated its use in a wide field, especially in the detection of "missing elements" in the periodic system. Attempts to make the analyses quantitative however have not so far been so successful owing to the complex nature of the phenomena involved.

The general method employed in the quantitative analysis of a substance is the determination of the intensities of corresponding lines of the elements present in the emission spectrum of a sample of the substance, which is made to function as the anticathode in an X-ray tube. In order to determine the relative amounts of the different elements present from the intensity data obtained it is necessary to assume the following: that under equal exciting conditions corresponding lines in the same series of different atomic spectra appear in an intensity ratio corresponding to the atomic concentrations of the sample on the anticathode. The chief sources of error encountered in this emission method are set out in a paper by Glocker and Frohnmayer.[2]

Some previous workers[3] have obtained anomalous values for the intensities of the characteristic radiation measured. These results cannot be explained satisfactorily either by supposing vaporisation of one or more constituents from the anticathode, or by errors arising from the methods employed in the determination of the line intensities. These anomalous intensity ratios would appear to be due to the absorption of the characteristic radiation of one element by another on the anticathode. This absorption effect will occur whenever there are present on the anticathode two elements such that the characteristic radiation of one falls within the absorption region of the other.

Theoretical

It may be assumed that the energy of an X-ray line is proportional to the number of atoms of the corresponding element on the anticathode. This may be written as follows:—

$$E_a = m.c_a$$

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[1] Phil. Mag., **26**, 1024 (1913); **27**, 703 (1914).

[2] Ann. Physik, **76**, 369 (1925).

[3] H. Stintzing: Z. physik. Chem., **108**, 51 (1923); Coster and Nishina: Chem. News, **130**, 179 (1925); Gunter and Stranski: Z. physik. Chem., **118**, 257 (1925); Gunter and Wilke: **119**, 219 (1926).

The proportionality between energy and concentration would hold for all kinds of atoms and is a general expression. In the particular case of two atoms adjacent to one another in the periodic system it is possible to carry this relationship a step further. Such atoms would have very similar inner electron systems and consequently the energy relationship for the same lines in their respective spectra, under equal exciting conditions, will be given by:—

$$\frac{E_1}{E_2} = \frac{\text{No. of atoms of } 1.}{\text{No. of atoms of } 2.}$$

The intensity of a line is a measure of the energy of the line. Thus the intensity of a given spectral line is proportional to the atomic concentration of the element emitting the line. In the special case of two elements adjacent in the periodic system the relationship given above will, under equal exciting conditions, hold for the ratio of the intensities.

There remains to be considered the effect of the applied voltage upon the line intensity. Webster and Clark[1] found that the intensity of a given line was proportional to the 3/2 power of the difference between the applied voltage and the critical exciting tension of the series of the element under consideration.

$$I = \text{Constant } (V - V_{min})^{3/2}$$

Whether this relationship is general or only applies to the elements investigated by Webster and Clark is open to question.[2]

From the above work however it may be assumed that the intensity is proportional to some function of the difference between the applied voltage and the critical exciting voltage.

$$I \propto f[(V - V_{min})]$$

Taking the case of two elements radiating under constant exciting conditions, it is seen that the intensity relationship of the spectral lines in the characteristic radiation of these elements will be constant.

$$\frac{I_1}{I_2} = \frac{K_1.f.(V - V_{min.})}{K_2.f.(V - V_{min.})} \text{ or } = \frac{K_1(V - V_{min.})^n}{K_2(V - V_{min.})^n}$$

All the expressions in the right hand side of the equation are constant so that

$$\frac{I_1}{I_2} = K.$$

The applied voltage then does not alter the relationship between intensity and concentration, provided that it is kept constant. Thus it is possible to write for any two elements

$$\frac{I_1}{I_2} = K.\frac{C_1}{C_2}$$

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[1] Phys. Rev., (2) 9, 571 (1917).

[2] Cf. Eddy and Laby: Proc. Roy. Soc., 127A, 22 (1930) where reference to other relationships is given.

where I_1 and I_2 are the intensities of the same line in the same series of the characteristic spectra of the two elements. The above is only true when neither of the elements absorbs the characteristic radiation of the other. Whether absorption occurs or not, the most general equation connecting intensity and atomic concentration is the following

$$I_1 = M_1 . C_1$$

In the special case of two elements adjacent to one another in the periodic system, the minimum critical exciting voltages of the two are almost equal. If a sufficiently high voltage be applied to the tube so that the difference between the applied voltage and the critical exciting voltage of either element is large in comparison to the difference between the critical exciting voltages of the elements, then we have

$$\frac{I_1}{I_2} = \frac{K(V - V_{\text{min.}})^n}{K(V - V_{\text{min.}})_2^n} \hat{=} 1$$

Considering these two elements together on the anticathode, the following intensity concentration relationship would hold for similar lines of their emission spectrum.

$$\frac{I_1}{I_2} = \frac{C_1}{C_2}$$

Of all possible methods of carrying out quantitative analysis by means of X-ray spectra the simplest is the Emission method. This is by a direct measurement of the intensities of the lines of the characteristic radiations of the elements on the anticathode. As has been seen the intensity of a given line in the emission spectrum is proportional to the number of atoms emitting that line. So that if the proportionality factor be known it is possible to determine the number of atoms present.

In the emission method the question of absorption arises. Where there are present on the anticathode two elements, such that the lines in the emission spectrum of one falls within the absorption region of the other then absorption will occur. Also a strengthening of the radiation of the absorbing element will take place owing to the emission of secondary or "fluorescent" radiation.

In the present work alloys of copper and silver and copper and zinc are used, and measurements of the intensities of the $K\alpha$ radiations made. Taking a mean value for the wavelengths we have the following values

	$K\alpha_{2.1}$
Silver	0.560 A°
Zinc	1.445 A°
Copper	1.539 A°

The absorption limits are as follows:

Zinc	1.296 A°
Copper	1.379 A°

From these figures it is seen that the $K\alpha_{2.1}$ line of silver falls within the absorption region of copper, as also does the weaker $K\beta$ silver radiation. This silver radiation will be partially absorbed and its intensity suffer diminution. The intensity of the copper radiation however will be strengthened by the addition of the secondary Cu radiation set up by the absorbed Ag radiation. Copper and silver therefore afford a very good example of this absorption effect.

In the case of the copper-zinc alloys no absorption of the $K\alpha_{2.1}$ zinc line occurs, and hence the mixture approximates to the conditions where two elements adjacent to one another in the periodic system are excited to emit radiation. Thus the copper-zinc concentrations can be directly deduced from the intensity ratios, the line intensities being in the same ratio as the atomic concentrations of the respective elements.

Vaporisation yet remains to be considered. This is the most serious difficulty that is to be met with in the emission method. Previous workers have attempted to eliminate this source of error by keeping the current passing through the tube as small as possible, in order to minimise heat effects, and by embedding the analysed substance in a non-volatile medium. By the use of alloys however the trouble of volatilisation is almost entirely eliminated. With long exposures however in the case of the copper-zinc alloys, the well known zinc volatilisation occurs.

All photographic methods used in the determination of the intensities of X-ray spectral lines are, on account of the shape of the blackening curve, liable to introduce error. In the present work this source of error is eliminated by measuring the intensities of the lines by means of the ionisation produced by their passage through a gas. The method however suffers from the drawback that it is not as sensitive as the photographic method, and that it requires a relatively intense beam to produce any marked ionisation effect. For this reason it was found to be impossible to make any measurements, using the ionisation method, on a mixture of oxides or on a mineral.

Another method of measuring the intensities was devised by the authors. It is a photographic method; but it does not depend on the estimation of the blackening of a photographic film. A wedge-shaped piece of aluminium is placed in front of the photographic film in the camera. Lines will be obtained on the film whose height will depend on the thickness of aluminium that each particular beam has been able to penetrate. By a measurement of the height of these lines and a knowledge of the dimensions of the wedge, the thicknesses of aluminium that the various lines have penetrated can be calculated. It must be assumed that where the film has just ceased to be affected, that is at the top of the line, the intensity of any given line radiation is constant. This means that the intensity of a beam of any given wavelength required just to affect a photographic film is a constant quantity for the type of film used.

That is I_A = Constant.

Then for any given wavelength, applying the well-known absorption equation

$$I = I_0 e^{-\lambda d}.$$

We have

$$I_0 = I_A.e^{+\lambda d} = \text{Constant. } e^{+\lambda d}$$

λ is known and d can be calculated from the height of the line obtained. Thus with a knowledge of the constant the line intensity can be calculated.

Considering two lines—for example Cu Kα_2 and Zn Kα_2—the ratio of their intensities will be given by the following expression

$$\frac{I_{0Cu}}{I_{0Zn}} = \text{Constant. } e^{(\lambda_{Cu}d_{Cu}-\lambda_{Zn}d_{Zn})}$$

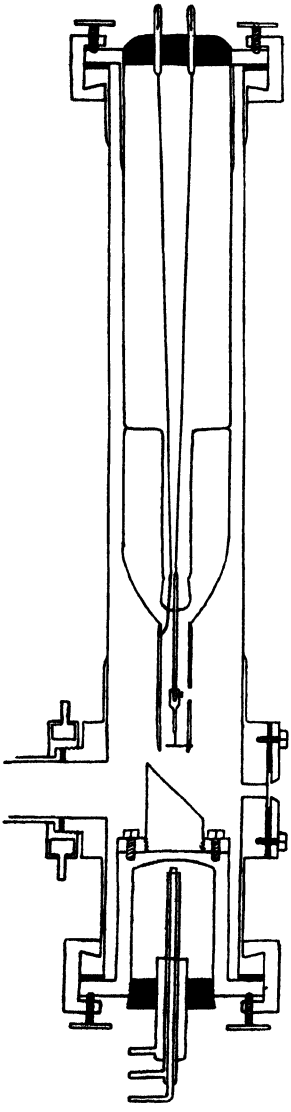

FIG. 1

Apparatus and Experimental Procedure

For this work it is essential to have an X-ray tube that gives a constant output. It is necessary that the potential across the tube remains constant for the whole series of readings, and that during the time taken for a set of readings on a particular alloy the current passing through the tube must also remain constant.

The X-ray tube used in these experiments is a modified form of Seeman Philips tube of the hot cathode or Coolidge type. The body of the tube is constructed of a special steel having the same coefficient of expansion as glass. Connection to the glass walls of the tube is made by direct fusion. Both cathode and anticathode are detachable. Gas-tight joints are made by means of rubber washers between machined faces. The tube is shown diagrammatically in Fig. 1. The anticathode consists of two parts, the body, constructed of bronze and hollow to allow of water cooling, and the cap. This latter is held in position by means of three small bolts. In this way the cap is kept in close contact with the body of the anticathode and does not suffer overheating. The cap consists of two parts, the target constructed out of the alloy under investigation, and the base of brass. The target is screwed into the base allowing good heat conduction. It is essential that the anticathode be efficiently cooled, and for this purpose a special water-cooler was devised. The water is directed in the form of a squirt directly on the underside of the anticathode. With an ordinary flow of water it is almost certain that a cushion of steam will form between the underside of the target and the cooling water. This cushion being a relatively poor conductor of heat will cause overheating of the anticathode with consequent volatilisation, sputtering, and pitting of the surface The present cooling device consists of three concentric tubes The innermost tube is an auxiliary outlet, the volume of water flowing out of which may be controlled by a screw clip, which carries away any steam that may be formed. The middle tube is the water inlet. The difference in diameters of these two tubes is small so that the water is squirted on to the underside of the target. The outer tube is shorter and wider and is the water outlet. The cooler is constructed of brass tubing and held in the anticathode by means of a rubber bung.

The alloys were made by heating together the constituent metals in approximately the correct proportions in a small furnace. A layer of borax was placed on top of the metals to act as a flux and to dissolve out any oxide formed. When the mixture was molten it was well stirred with a carbon rod and cast into a piece of steel tube that had been covered internally with graphite. The cylinders of alloys so obtained were turned down to the required dimensions and cut at 45°. Since the X-ray analysis does not give a high degree of accuracy it was considered sufficient to analyse for one constituent only of the alloys. The copper-silver alloys were analysed for silver by means of a gravimetric estimation of silver chloride. The copper-zinc alloys were analysed for copper electrolytically.

The X-ray tube was continuously evacuated by means of a Leybolt three-stage mercury diffusion pump, backed by a two stage large capacity rotary oil pump. An estimate of the state of the vacuum was obtained by means of a McLeod gauge in the system. The requisite potential for working the tube was generated by an induction coil. One side of the secondary of the coil was earthed, the other connection to the cathode of the tube. The anticathode was earthed, and an alternate spark gap connected across the tube. An energy input of 0.77 kilowatts was supplied to the coil, and the exciting voltage of the tube was 40,000 volts. The filament was heated by an insulated bank of accumulators of large capacity giving a total of 16 volts. The filament current was 4.6 amperes. The filament current was found to be very critical.

The spectrometer used in these experiments was a standard Bragg type supplied by Messrs Pye. A calcite crystal was used and the angles of the crystal table and ionisation chamber calculated from the wavelength and lattice constant data. Measurements were made on the first order Kα radiations, the α_2 and α_1 not being resolvable. A modified type of Tilting Electroscope was used to measure the ionisation produced, a description of which is given in a paper by H. A. Bumstead.[1] The ionisation chamber was charged to a potential of +200 volts, and the two plates of the electroscope to +200 and −200 volts. Under these conditions and using a gold leaf of width not greater than 0.05 cm. a sensitivity of 25 scale divisions for 0.1 v. was obtained. The gas used in the ionisation chamber was dry sulphur dioxide. This was obtained from a siphon and passed over P_2O_5 before use. In practice it was found necessary to recharge the chamber with gas for every set of readings. The electroscope leaf was timed, by means of a metronome, over 10 or 30 scale divisions depending on the intensity of the beam and the sensitivity of the electroscope. The metronome was set to 100 beats per minute. Care had to be taken to earth shield the electroscope and connections against stray electrical effects.

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[1] Am. J. Sci., December (1911).

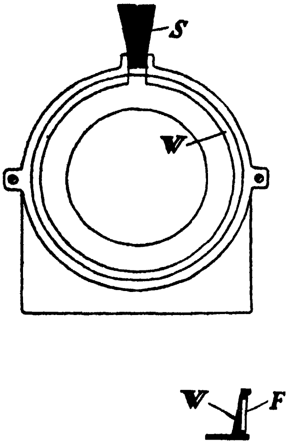


FIG. 2

The wedge camera consists of a Debye camera of diameter 10 cms. fitted with an aluminium wedge around its circumference. This is best seen by reference to Fig. 2. The wedge (W) is made by driving to fit inside the circular film holder. The dimensions of the wedge will depend on the wavelength of the radiation used. For copper K radiation it was made 0.15 cms. at the base tapering off to zero at the top—the height of the wedge being 1.81 cms. These dimensions gave lines of the correct magnitude with an exposure of 4 hours The slit (S) is a line slit, extending the height of the film in order to obtain an even intensity distribution throughout each reflected beam. The wedge camera was used in a Müller spectrograph. A calcite crystal rocked through a small angle was used to analyse the beam.

Experimental Results

1. *Copper-Silver Alloys.*

Intensity measurements by ionisation method. In order to obtain the correct values for the intensity ratios of the copper and silver lines it is necessary to

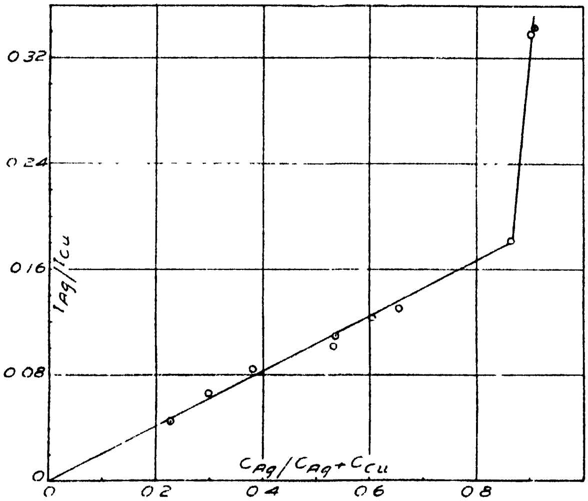
TABLE I

% Composition		Measured Intensity Ratio		Corrected Intensity Ratio		$\frac{C_{Ag}^*}{C_{Ag} + C_{Cu}}$	$\frac{I_{Ag}}{I_{Cu}}$
Ag	Cu	Ag	Cu	Ag	Cu		
94.5	5.5	1	1.52	1	2.90	0.908	0.345
93.9	6.1	1	1.58	1	2.94	0.903	0.340
91.8	8.2	1	2.95	1	5.50	0.865	0.182
76.3	23.7	1	4.10	1	7.63	0.655	0.137
72.2	27.8	1	4.35	1	8.10	0.605	0.124
66.2	33.8	1	4.84	1	9.02	0.535	0.111
65.9	34.1	1	5.25	1	9.78	0.532	0.102
50.2	49.8	1	6.30	1	11.7	0.380	0.0853
41.6	58.4	1	8.06	1	15.0	0.296	0.0666
32.7	67.3	1	11.85	1	22.1	0.227	0.0453

* C_{Ag} = Concentration silver in gm. mols.
C_{Cu} = Concentration copper in gm. mols.

correct the observed intensity values for absorption in the aluminium windows of the X-ray tube and ionisation chamber, and also for absorption in the air space between the X-ray tube and the chamber.

The total thickness of aluminium passed through is 0.0051 cms., and the length of air traversed is 30 cms. This gives a correction factor of ×1.37 for the aluminium, and ×1.36 for the air.



Graph I

Copper-Silver Alloys

As is seen from the graph the following relationship between relative intensity and atomic concentration holds over a large concentration range

$$\frac{I_{Ag}}{I_{Cu}} = \frac{M.C_{Ag}}{C_{Ag} + C_{Cu}}$$

2. *Copper-Zinc Alloys.*

Intensity measurements by ionisation method. As in the case of the copper-silver alloys a correction must be applied for the absorption that occurs in the aluminium windows. In this case however the wavelength difference is sufficiently small that the different absorptive powers of the air traversed in the spectrometer can be neglected. The correction factor of the aluminium is ×1.12.

Table II

% Composition		Measured Intensity Ratio		Corrected Intensity Ratio		Composition in Gm. Mols	
Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu
40.15	59.85	1	1.48	1	1.66	1	1.53
48.15	51.85	1	0.84	1	0.94	1	1.11

Intensity measurements by wedge camera method. In the circular camera the top of the wedge is masked by the top flange of the camera for a distance of 0.25 cm. This length therefore must be added to the measured lengths of the lines in order to obtain the correct length. The thickness of the aluminium window of the X-ray tube (0.0025 cm.) is added to the thickness of aluminium penetrated calculated from the height of the lines.

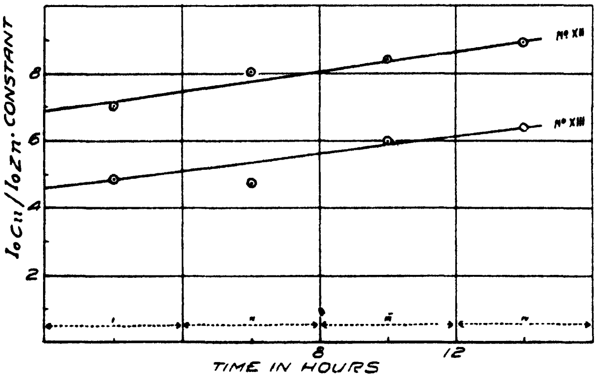
TABLE III

Alloy No. XII 40.15% Zn 59.85% Cu
Alloy No. XIII 48.15% Zn 51.85% Cu

Four exposures each of four hours' duration were made with each alloy.

Exposure	Line Measured	Measured Length of Line on Film		Calculated Thickness Al Penetrated		$\lambda_{Cu}d_{Cu}-\lambda_{Zn}d_{Zn}$	$\frac{K.I_{oCu}}{I_{oZn}}$
		Cu	Zn	Cu	Zn		
				Alloy XII			
1.	$K\alpha_2$	0.295	0.200	0.048	0.040	1.924	6.9
	$K\alpha_1$	0.260	0.150	0.045	0.036	1.960	7.1
2.	$K\alpha_2$	0.300	0.200	0.049	0.040	2.05	7.8
	$K\alpha_1$	0.290	0.175	0.048	0.038	2.12	8.3
3.	$K\alpha_2$	0.300	0.200	0.049	0.040	2.05	7.8
	$K\alpha_1$	0.280	0.150	0.047	0.036	2.20	9.0
4.	$K\alpha_2$	0.310	0.175	0.049	0.038	2.27	9.6
	$K\alpha_1$	0.280	0.160	0.047	0.037	2.11	8.2
				Alloy XIII			
1.	$K\alpha_2$	0.275	0.225	0.047	0.042	1.58	4.85
	$K\alpha_1$	0.250		0.045	——	——	——
2.	$K\alpha_2$	0.300	0.250	0.049	0.045	1.52	4.56
	$K\alpha_1$	0.275	0.230	0.047	0.042	1.58	4.85
3.	$K\alpha_2$	0.275	0.200	0.047	0.040	1.79	5.99
	$K\alpha_1$	0.275		0.047			
4.	$K\alpha_2$	0.200	0.100	0.040	0.031	1.85	6.37
	$K\alpha_1$	0.200		0.040			

During the measurements it was noticed from the condition of the X-ray tube that a certain amount of zinc volatilisation was taking place. From the experimental results it is seen that a progressive amount has taken place, causing, in both cases, a steady increase in the concentration of the copper and hence an increase in the intensity ratio. In order to correct for this progressive increase and to obtain the intensity ratio given by the alloy before volatilisation occurred, the intensity ratios were plotted against the time of exposure. For a four hour exposure the resulting intensity ratio is the average of the intensity ratios over that period. The intensity ratios therefore were plotted at 2 hrs., 6 hrs., 10 hrs., and 14 hrs. Extrapolating these values back to zero time gives the correct intensity ratio. It was necessary to assume a linear relationship between volatilisation and time of exposure.



GRAPH II

Copper-Zinc Alloys. Extrapolation of Intensity Ratios

Extrapolated Intensity Ratios from Graph.

Alloy No.	K.I$_0$Cu/I$_0$Zn
XII.	6.9
XIII.	4.6

Putting 4.35 for the value of the constant K, we have the following values for the intensity ratios

XII.	1.59
XIII.	1.06

TABLE IV

% Composition		Composition in Gm. Mols		Intensity Ratio Ionisation Method		Intensity Ratio Wedge Camera Method	
Zn.	Cu.	Zn.	Cu.	Zn.	Cu.	Zn.	Cu.
40.15	59.85	1	1.53	1	1.66	1	1.59
48.15	51.85	1	1.11	1	0.94	1	1.06

Conclusions

The results obtained demonstrate two different phenomena that are to be met in the direct emission method of quantitative X-ray analysis. The copper-silver alloys offer a good example of two elements that are such that one absorbs the radiation of the other. The copper-zinc alloys exhibit no such absorption, and are an example of the simpler type where one is dealing with two elements adjacent to one another in the periodic system.

Considering firstly the results obtained from the measurements of the copper-silver alloys. It is seen that the intensity ratio is directly proportional to the ratio of the silver concentration expressed in gm. mols. to the total number of gm. mols. of silver and copper present.

This may be expressed

$$I_{Ag}/I_{Cu} = M.C_{Ag}/C_{Ag}+C_{Cu}$$

The wavelength of the line of shortest wavelength in the K series of copper is greater than the wavelength of the Kα_2 line of silver, so that the energy of the Kα_2 line is greater than the energy required to excite the K series of copper. Hence in accordance with Stokes law secondary or fluorescent radiation will be produced. The absorbed silver radiation will give rise to secondary K radiation of copper. Thus the silver intensity, diminished by absorption, will be some function of the silver concentration, whilst the copper intensity, augmented by secondary Cu radiation, will be a function of both the copper and the silver concentrations.

The high values obtained with very low concentrations of copper may be accounted for by assuming that the number of copper atoms present are insufficient to absorb the optimum quantity of the emitted silver radiation.

The copper-zinc alloys behave in a normal manner and demonstrate the possibility of quantitative X-ray analysis of metallic alloys. The conditions that must be observed in order that the composition of a mixture may be directly determined quantitatively from the intensities of the lines in its emission spectrum are then the following:

The elements are adjacent to one another in the periodic system.

The emission spectrum of any constituent element must not fall within the absorption region of any other.

The measurement of the relative intensities of the lines in the emission spectra by means of the ionisation of a gas overcomes many of the difficulties inherent in any photographic method, especially that of estimating the blackening produced. The ionisation method however suffers from the disadvantage that it requires a relatively intense X-ray beam.

From the results obtained with the "wedge" camera the following conclusions can be drawn.

The relative intensities of similar lines in emission spectra can be determined by a measurement of their penetration of a wedge of aluminium, the depth of penetration being given by the length line received on a photographic film behind the wedge.

When dealing with lines of different wavelength it is necessary to introduce a constant to correct for change of photographic effect with wavelength.

Summary

1. The relative intensities of the K lines in the characteristic X-ray emission spectra of copper-silver alloys have been determined by measurement of their ionising powers.

The following relationship between intensity and atomic concentration has been found to hold:

$$\frac{I_{Ag}}{I_{Cu}} = \frac{M.C_{Ag}}{C_{Ag} + C_{Cu}}$$

The silver radiation suffers partial absorption in the copper and gives rise thereby to secondary copper radiation, thus diminishing the silver radiation and augmenting the copper.

2. Copper-zinc alloys have been similarly investigated. A linear relationship between relative intensity and atomic concentration has been found to hold.

3. A method for the determination of relative intensities of lines in an X-ray spectrum, dependent on the measurement of their penetration of an aluminium wedge, has been devised. The copper-zinc alloys were also investigated by this method.

The Sir William Ramsay Laboratories of Inorganic
and Physical Chemistry,
University College, London.
September 8, 1930.

THE "THERMO-SENESCENCE EFFECT" EXHIBITED BY GOLD SOLS AT ELEVATED TEMPERATURES, AND "AGEING" AT ROOM TEMPERATURE*

BY EMLYN JONES AND W. C. M. LEWIS

Introduction

The present investigation has been carried out with the object of investigating further the change in behaviour—with respect to the rate of coagulation—which is exhibited by gold sols as a consequence of the sol having been maintained at a high temperature, namely 80°C., before addition of the coagulating agent.

The maintenance of the sol at 80°C. for approximately three hours has been shown by previous workers in this Laboratory (Miss A. Davies,[1] P. J. R. Butler[2]) to give rise to a sol which has reached a colloid equilibrium or steady state. The process of attainment of this state has been termed thermo-senescence. It is only with material which has undergone preliminary treatment of this kind that reproducible values for the Smoluchowski coagulation coefficient can be obtained. The value of this coefficient can therefore be employed, other conditions being maintained constant, as a precise means of determining to what extent the thermo-senescence process has been controlled.

It will be convenient at this point to recall the definition of the coefficient as it appears in Smoluchowski's[3] theory of coagulation of colloids by an electrolyte.

For the case in which the coagulation is "rapid," that is, the rate is independent of further increase in concentration of coagulating electrolyte. Smoluchowski's theory leads to the expression

$$\nu_1 = \frac{\nu_0}{(1 + \beta_0\, t)^2}$$

where β_0 is the coefficient for the conditions referred to, ν_0 = the initial number of primary particles, and ν_1 = the number of primary particles remaining after time "t."

$$\beta_0 = 4\,\pi\,D\,\rho\,\nu_0$$

where ρ = the radius of the sphere of attraction of a primary particle, and D = the diffusion constant as given by Einstein's equation, viz.

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r},$$

where r = the radius of the particle and η = the viscosity of the medium.

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* From the Muspratt Laboratory of Physical and Electro-chemistry, University of Liverpool.

[1] A. Davies: J. Phys. Chem., 33, 274 (1929).

[2] Butler: J. Phys. Chem., 34, 656 (1930).

[3] Smoluchowski: Z. physik. Chem., 92, 129 (1917).

Smoluchowski attempted to modify his theory so as to include the case where the coagulation velocity is dependent upon the concentration of electrolyte, i.e. the slow region of coagulation. In this region owing to incomplete neutralisation of the electric charge on the particles the attractive forces are not at their maximum. Thus every collision does not lead to a permanent aggregation but only a certain fraction of them. A probability factor ξ was, therefore, introduced to allow for this, the resulting equation being

$$\nu_1 = \frac{\nu_0}{(1 + \xi\, \beta_0\, t)^2}$$

ξ, being a function of the residual net charge on the particle, will be constant throughout the course of the coagulation only on the assumption that the particles are equally charged, an assumption apparently not justified in practice, cf. Miss Garner.[1] Setting $\xi\, \beta_0 = \beta$ we obtain, for the region of slow coagulation

$$\nu_1 = \frac{\nu_0}{(1 + \beta t)^2} \text{ or } \beta = \frac{1}{t}\left(\sqrt{\frac{\nu_0}{\nu_1}} - 1\right)$$

β is therefore the rate of variation of $\left(\sqrt{\frac{\nu_0}{\nu_1}} - 1\right)$ with time, and if this expression be plotted against the time "t," β at any instant will be given by the tangent to the resulting curve.

If β be a true constant the relation should be linear with its origin at zero time. Miss Garner, *loc. cit.*, using gold sols which had undergone the preliminary thermo-senescence treatment, found that the relation was linear over a considerable portion of the time interval employed, but that, on being extrapolated backwards, the line did not pass through the origin. This "zero discrepancy" as it has been termed by Miss Garner, is due to the fact that, although over a major portion of the reaction the velocity coefficient of coagulation is constant, during a short initial period the velocity is enhanced. In other words a fraction of the primaries coagulate much more rapidly than do the majority of the particles. This has been explained as being due to the particles of the sol being unequally charged to begin with.

To return to the thermo-senescence phenomenon itself. This effect was first recognised in the case of colloidal material coagulated under slow conditions. The effect was always in the direction of a decrease in the value of β as compared with material which had not undergone thermal treatment. In other words thermo-senescence *increases* the stability of the sol. This has been ascribed by Miss Davies, *loc. cit.*, to an actual contraction of the initial particles with the result that the charge density increases and the rate of coagulation (in the slow region) is rendered still slower.

More recently, Butler, *loc. cit.*, has found the phenomenon to exist when the concentration of electrolyte is such as to ensure rapid conditions. Combining the results of both investigators the most probable explanation is that high temperature causes a contraction in the size of the primaries. In the case of slow coagulation this causes an increase in charge density which would give rise to a slower rate of coagulation. In the case of the rapid region the particles are completely discharged and the contraction of the particle acts to give rise to a decrease in ρ, the radius of attraction of the particle, which in turn decreases the probability of collision between the uncharged particles, thereby leading to a less rapid rate of coagulation.

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[1] Garner: J. Phys. Chem., **30**, 1410 (1926).

Although the theory advanced to account for thermo-senescence, namely contraction of the particle, is logical enough, it is clear that other explanations might be put forward. The most obvious of these would be to attribute the influence of temperature to removal of impurities, themselves electrically charged. It was the main purpose of the experiments described in the present paper to test this possibility by endeavouring to get rid of such impurities by dialysis prolonged far beyond the usual 3 to 4 days normally given to "remove impurities," and then to see if the thermo-senescence phenomenon was modified thereby.

Experimental

The gold sol was prepared by the "Acetone" reduction method adopted by Miss Davies, *loc. cit.* The method consists in adding to 480 ccs. of redistilled water, 5 ccs. of a 1.2 percent solution of gold chloride together with 14 ccs. of a 0.18 N potassium carbonate solution, and 3 ccs. of acetone. On warming the mixture a pinkish tinge appears which deepens as the temperature rises. The solution is allowed to boil vigorously for about three minutes. A clear ruby-red sol results. A number of these preparations were made and mixed to form one large volume of sol.

All vessels and containers with which the sols come in contact were of quartz. These were thoroughly cleaned before use with alkali, alcohol-nitric acid mixture, distilled water, and finally steamed out for five minutes with steam from redistilled water. In the present investigation the sol was diluted with redistilled water. The original sol contained about 56 mgs. of gold per litre. The dilution employed was 1 part of sol to 1 part of water.

The apparatus employed for the continuous dialysis of the gold sol simply consisted of a series of collodion sacs containing the gold sol. These were surrounded by a continuous stream of distilled water. The collodion sacs, having a capacity of over 300 ccs. were mounted on wide rubber bungs and were made air-tight. A stream of nitrogen was passed periodically through the whole series of sacs. Such an arrangement ensured that the sol was never in contact with the air during the dialysis. Samples of the sol were syphoned out at various time intervals by means of a syphon tube leading in to each sac. A sheet of wood covered each of the beakers containing the distilled water. In this sheet, holes were bored of sufficient size to allow of the support of the sacs and the entrance and exit of the distilled water which passed through the whole series of beakers by means of a series of syphon tubes. The water was, therefore, kept free from dust and metallic particles which may have been present in the atmosphere. From the last beaker of the series the water passed to another vessel from which there was an overflow and the level of the distilled water throughout the apparatus was regulated by varying the level of this outlet. The dialysis operation was carried out at room temperature.

In order to find the mean rate of coagulation in the slow region the technique employed by Butler, *loc. cit.*, was used as it ensures greater reproducibility and more controllable conditions than were possible in the methods employed by other workers.

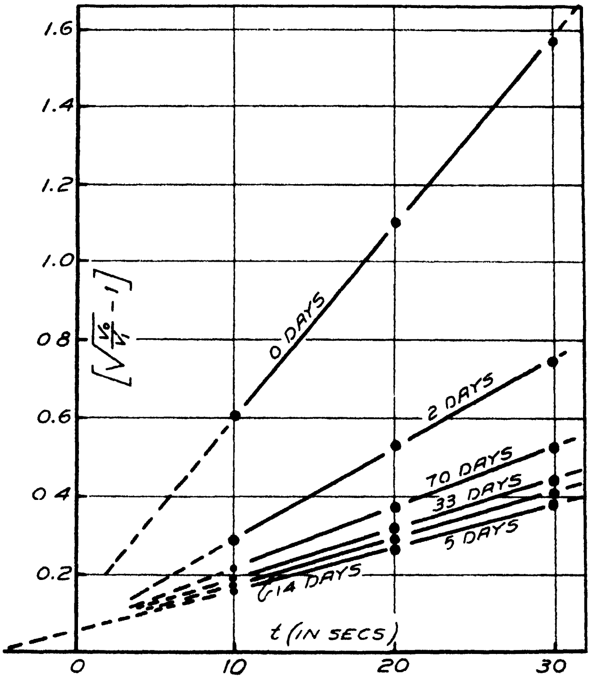

Fig. 1

50 ccs. samples of the sol were syphoned out at various time intervals during the dialysis. Each sample was then made up to 100 ccs. with redistilled water. The samples were then raised to and maintained at 80°C. In order to initiate the actual coagulation process (carried out at 80°C.) 2 ccs. of a 0.0664 N $BaCl_2$ was added. This on addition to the sol gave a concentration of 0.00133 N which concentration gave a slow rate of coagulation. The coagulation was arrested by adding 2 ccs. of a 2% gelatin solution and shaking. It has been found that the flasks containing the sol sample have to be immersed in the thermostat at 80°C. for half an hour before they attain this temperature and this was taken as the zero time for the "duration of heat treatment." The sol samples were then maintained at this temperature for 1 hour and 3 hours respectively before initiating the coagulating process.

In the present investigation the extent of coagulation was determined after 10, 20, and 30 secs. respectively. The Hatschek[1] wedge method as modified by Butler, *loc. cit.*, was employed.

Table I summarises the results obtained. The "duration of heat treatment" refers to the time during which the sol is maintained at 80°C. prior to the initiation of the coagulation process at 80°C. The β values are obtained from the slope of the curve as previously described. The accompanying graph serves to illustrate some of the results obtained, namely those obtained for the various periods of dialysis after three hours heat treatment.

TABLE I

Period of Dialysis	Duration of heat treatment	β
0 Days	1 Hour	0.0352
"	3 Hours	0.0493
2 Days	1 Hour	0.0234
"	3 Hours	0.0217
5 Days	1 Hour	0.0149
"	3 Hours	0.0112
14 Days	1 Hour	0.0152
"	3 Hours	0.0122
33 Days	1 Hour	0 0154
"	3 Hours	0.0128
70 Days	1 Hour	0.0186
"	3 Hours	0.0157

Discussion of Results

The results given in the table demonstrate the existence of two distinct phenomena.

In the first place on comparing the β values obtained after heat treatment for 1 hour and 3 hours respectively, it will be observed that in all cases (except the case in which the sol was completely undialysed) there is a diminution in the coagulation coefficient, the value recorded after 3 hours heat treatment being, in fact, an equilibrium or limiting value. This behaviour is exhibited by material which has been dialysed (at room temperature) over very different periods of time, from two days to as much as seventy days. This phenomenon, namely, a *fall* in β to a limiting value, as a result of heat treatment, is the true thermo-senescence phenomenon, i.e. an increased stability. In the second place the results show that dialysis, when prolonged, has the effect of *increasing* β. This effect manifests itself after a dialysis of 5 days duration and goes on increasing up to 70 days, the farthest point investigated. In other words, after a few days dialysis at room temperature further treatment is accompanied by a decrease in the stability of the sol. This phenomenon most closely resembles that to which the term "ageing" has very generally been given.

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[1] **Hatschek: Trans. Faraday Soc., 17,** 499 (1921).

It may be recalled that the earlier work from this laboratory led to the conclusion that thermo-senescence is due essentially to a contraction of the individual sol particle whereby its range of attraction is diminished and, if it be charged at all, its charge density is increased. On the other hand, it is generally assumed that the decreased stability associated with ageing (at ordinary temperature) has its origin in a redistribution of adsorption effects on the part of the electrolytic "impurities" present in the sol system.

Until the results just given had been obtained, it was not clear whether heat treatment led in the same direction as the effect of mere passage of time. It now appears that the two effects do not necessarily operate in the same direction. In the light of this conclusion the term thermo-senescence is perhaps not particularly suitable but we have retained its use as it is unlikely to lead to ambiguity.

As a practical point the results obtained lead to the conclusion that in general no sol is in a suitable state for examination until it has been dialysed for about 4-5 days and has then been subjected to about 3 hours heat treatment.

Summary

Instead of the usual three to four days dialysis, gold sol has been subjected to prolonged dialysis (up to 70 days) and examined for the thermo-senescence phenomenon. This was found to be exhibited in all cases as a real and definite phenomenon, which fact renders the view that thermo-senescence may be attributed to the further removal of impurities, invalid. The conclusion already arrived at that thermo-senescence is due to contraction of the sol particles as a result of raising the temperature seems still to be the most probable explanation of the phenomenon. Incidentally the investigation has served to demonstrate the existence of the ordinary ageing effect at room temperature. The ageing effect decreases the stability of the sol as shown by the increase in the coefficient β. The ageing effect may well be attributed to ionic adsorptions and desorptions. The thermo-senescence effect on the other hand decreases β, that is increases the stability of the sol. The two phenomena, namely thermo-senescence, and slow ageing at ordinary temperatures, are therefore distinct phenomena.

The authors desire to express their thanks to Imperial Chemical Industries, Ltd. for a Grant to the Department of Physical Chemistry of this University.

Liverpool,
October, 1930.

ON PHENYLACETALDEHYDE AND ITS POLYMERISATION

BY JAMES ROBERT POUND

It is known that phenylacetaldehyde polymerises easily, especially on contact with air and light. Enklaar[1] kept a specimen in the dark for six months and found it had then polymerised to the extent of nearly one-half; finally he obtained a crystalline solid, melting at 33°. A sample of phenylacetaldehyde was obtained by the writer from L. Givaudan and Co., France. The manufacturers state that storage in a stoppered bottle in a dark place reduces polymerisation and that the alcoholic solution keeps almost indefinitely. Our sample of phenylacetaldehyde was a colourless, sweet-smelling and fairly viscous liquid; it was kept corked in a dark cupboard and gradually became more viscous, and after 17 months small crystals appeared in the body of the liquid, though some crystals had formed above the liquid some months previously. The refractive index of the liquid increased with age, as well as its density and viscosity; these changes have been studied at room temperatures (7°-20°) and at 30°.

Some experiments were carried out with phenylacetaldehyde on watch-glasses, which were weighed from time to time. Though phenylacetaldehyde boils at about 200° and has a vapour pressure of 5 mm at 74.5° (Givaudan), it is sufficiently volatile to lose weight continuously when kept at room temperatures on watch-glasses in air or in closed vessels over sulphuric acid or calcium chloride or water. In all these experiments the decrease in weight falls off with age. When kept over sulphuric acid or calcium chloride, the phenylacetaldehyde vaporised is picked up by these reagents. In air and over sulphuric acid and calcium chloride, the phenylacetaldehyde becomes in time slightly yellow, covered with a skin or viscous surface-layer, develops crystals, and finally becomes a hard glassy mass: these changes proceed more rapidly over the desiccating agents; but the rate of loss of weight is approximately the same in all cases. When kept in a closed vessel over water, the phenylacetaldehyde does not become glassy hard or full of crystals, but it remains somewhat fluid and becomes opalescent with age: the loss of weight however is the same as before. This loss of weight depends on the room temperature and is due to simple evaporation. One sample, kept in the open air at an average temperature of 20°, lost in 150 days 14 per cent of its original weight: minute crystals were present in the liquid at the start of the experiment, were numerous after 30 days, and constituted the bulk of the mass, which was then slightly straw-coloured, after 90 days. Another sample of phenylacetaldehyde was placed in a flask and attached to a Lunge nitrometer containing mercury: after several days no absorption of oxygen was noticed. The flask was opened, a tube of calcium carbide was enclosed, and the whole system joined up again: after several weeks the volume of the gas in the system was unaltered. Thus no absorption of oxygen and no evolution of water vapour occurred.

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[1] J. Chem. Soc. Abs. A, 1926, 614.

The acidities of samples of the phenylacetaldehyde were determined by dissolving known weights in alcohol and titrating with carbonate-free alkali, using phenolphthalein as indicator: the end-points were sharp, and the acid was calculated as phenylacetic acid. The stock phenylacetaldehyde showed 1.1% acid. A sample dissolved in alcohol had air aspirated through it for 20 hours at 7° and then showed 1.8% acid. Another sample after exposure to air on a watch-glass for 56 days showed 2.3% acid; and that sample exposed to air for 150 days showed finally 2.0% acid: but the residues from the other watch-glass experiments (see above) showed lower '% acid'. A sample, III (see later), after keeping at 30° for 30 days showed 1.35% acid. Thus phenylacetaldehyde does not oxidise appreciably on exposure to the air.

The refractive index, *n*, was determined at 20° by a Hilger-Abbe refractometer, which gave results to the fourth decimal place for $n_D^{20^\circ}$. For the stock sample of phenylacetaldehyde, S, kept at room temperature, about 15°, the refractive index increased with age at a diminishing rate; but after crystals had formed, the refractive index of the liquid varied little: with this and other samples n actually diminished a little after crystals had separated, —indicating supersaturation: also just before crystals appeared, the 'line' in the refractometer was blurred, as it is with suspensions,—indicating incipient (liquid?) crystals. The refractive index is the most convenient property to indicate the age of phenylacetaldehyde; and crystals are about to form, polymerisation having progressed thus far, when $n_D^{20^\circ} = 1.570$ approximately. Some results for the stock sample, S, were:—

Age of sample (days)	0[x]	145	343	364	413[y]	563[z]	692
n_D^{20}	1.5564	1.5631	1.5700	1.5706	1.5709	1.5703	1.5730

Notes: [x] On first opening the stock bottle, 4 months after arrival in Ballarat.

[y] After small crystals had appeared.

[z] From only a thin layer of liquid above a paste of crystals. Between dates y and z, n lay between these values.

Part of the stock sample was distilled under reduced pressure, the B.P. rising somewhat throughout: the distillate, sample I, was kept at room temperature, say about 15°, for 85 days and the refractive index was determined from time to time, see Table and Graph. The refractive index increased throughout, and this sample never reached crystal-formation. The refractive index, like the density and the viscosity, changes somewhat abnormally with the fresh sample for the first few hours.

Another part of the stock sample was distilled under 79 mm pressure: a first fraction was discarded, and then was collected the main sample, III, boiling from 125° to 141°. This sample was divided into three lots which were kept at 30° for eighteen days and more. One lot was kept in a specific-gravity bottle, in which its density was determined at intervals, the bottle being filled up as required from the third lot. The second lot was kept in an Ostwald viscometer, closed with calcium chloride tubes, and the time of flow was found at intervals; from the contemporaneous values of the density the viscosities were calculated. After eighteen days the density of the liquid from the viscometer was 1.0855, while that in the specific gravity bottle was 1.0912 (both at 30°). The increases in density of the two lots were therefore not quite equal; but as the viscosity increases in this time to over twelve times its initial value, the errors introduced by taking the densities of the viscometer liquid as equal to those of the specific-gravity bottle liquid are negligible. For these reasons however the densities are only quoted to four decimal places and the viscosities to the third significant figure. From the third lot of the liquid the specific gravity bottle was filled up from time to time and samples were withdrawn for the refractive index determinations. In these samples kept at 30° crystals appeared in thirty days.

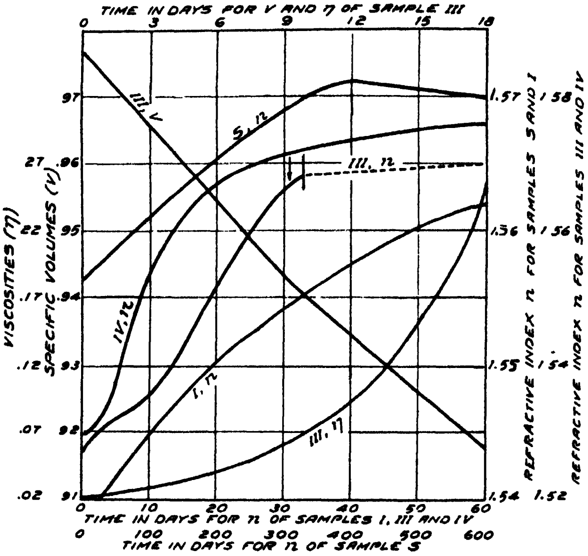

FIG. 1

Graph showing variation of properties of phenyl-acetaldehyde with lime

That part of samples I and III which remained after the experiments therewith, was redistilled and gave a sample IV of similar boiling point to III. Sample IV was kept at 30°, in two lots, for eighteen days, the density and refractive index being determined at intervals as before. The results obtained with the samples I, III and IV are given in the table and are plotted in the graph.

TABLE I

Table showing the Change of Properties of Phenylacetaldehyde with Time

Age of Sample	Sample I (kept at room temps)	Sample III (kept at 30°)			Sample IV (kept at 30°)	
	$n_D^{20^\circ}$	$n_D^{20^\circ}$	$D_{4^\circ}^{30^\circ}$	η^{30°	$n_D^{20^\circ}$	$D_{4^\circ}^{30^\circ}$
1 hour	1.5370	1.5272	1.0242	—	1.5295	—
5 hours	—	1.5282	—	.02044	1.5296	1.5275
1 day	—	1.5291	1.0274	.0220	—	—
3 days	1.5402	1.5310	1.0357	.0279	1.5339	1.0347
4 "	1.5411	1.5319	1.0398	.0313	—	—
6 "	1.5422	1.5329	1.0481	.0403	1.5431	1.0419
9 "	1.5444	1.5351	1.0597	.0603	1.5519	1.0488
12 "	1.5466	1.5390	1.0698	.0937	1.5578	1.0586
15 "	1.5481	1.5440	1.0783	.1503	1.5618	1.0716
17 "	1.5488	—	—	—	1.5649	1.0792
18 "	1.5492	1.5482	1.0912	.248	1.5654	—
20 "	1.0502	1.5510	1.0969	—	1.5670	
29 "	1.5540	1.5651	—	—	1.5713	
30 "	1.5543	1.5663	1.1160[x]	—	1.5716	
32 "	1.5550	1.5678[x]	—		1.5722	
40 "	1.5575	*1.5689[x]			1.5736	
47 "	1.5593	*1.5692[x]			1.5743[x]	
79 "	1.5658	*1.5723[x]			1.5762[x]	
85 "	1.5667	—			1.5767[x]	

[x] Crystals had formed here.
* This part of sample III was kept at room temperatures, say 20°, from the 32nd day.

The density increases linearly with the time and the specific-volume decreases linearly with the time; the density of sample IV increases less rapidly than that of sample III; and the mean density at time zero, $D_{4^\circ}^{30^\circ}$, is 1.026, and the density seems to rise less rapidly for the first few hours than it does afterwards. The fluidity-time curve is linear for the first few days, indicating $f_0 = 50.15$ or $\eta_0 = 0.01994$, and then the curve becomes convex to the time-axis. The viscosity-time curve is convex to the time-axis and becomes steeper with time. The (logarithm of the viscosity)–time curve is nearly linear; it is slightly convex to the time-axis, and when the time is large the ratio $\frac{\log \eta}{\text{time}}$ approaches a constant value. In general the refractive index-time curve is linear. However the refractive index, n, tends to rise abnormally rapidly at the start, that is just after the distillation of the sample. And the various n/time curves at last become concave to the time axis or the rate of increase of n slackens with the age of the specimen and becomes much less after crystals have formed. With sample III crystals appeared before the thirty-second day, when the n was 1.5678. The average rate of increase of n is 0.0015 at 30° and 0.00043 at 15°. It may also be concluded that the specific refractive power, $(n-1)/d$, does not vary much with the age of the sample.

The above results seem to indicate that the rate of formation of the polymerised phenylacetaldehyde is constant at the one temperature, and finally the crystalline polymer separates from the liquid. For the specific volumes of simple liquid mixtures are additive; and the refractive index is also an additive property. And many observers have concluded that the logarithm of the viscosity is an additive property,—see Arrhenius (1887) and Kendall and Monroe (1917). The rate of formation of the polymer is approximately three to four times faster at 30° than at 15°, which is about the normal result for a chemical change. But by distillation the unpolymerised liquid is again obtained. The rate of formation of the polymer doubtless is influenced too by the impurities in the liquid, such as traces of moisture and of acid and of other substances which were present to some extent in our samples, as well as by exposure to the light. In conclusion there seems little reason to doubt that the rate of formation of the polymer is constant under constant conditions.

The crystals of the polymerised phenylacetaldehyde were much less soluble in alcohol than the unchanged liquid. Thus the stock sample of phenylacetaldehyde, containing much polymer, was treated with alcohol and the residual crystals were washed with alcohol on a glass filter until they were free of the viscous mother-liquid, and then the crystals were dried in a desiccator over sulphuric acid. Two separate lots of the polymer, a white opaque, granular powder, were thus prepared: they proved to have identical properties. This polymer melted sharply at 104°: no water vapour was evolved on melting, and the fused mass cooled to a glassy hard solid. This polymer was soluble in hot alcohol or in excess of cold alcohol, insoluble in cold or boiling water, and was more or less soluble in petrol (gasoline; B.P. = 82°-98°), carbon tetrachloride, chlorobenzene, benzene, bromoform, ethylene chloride, ethylene bromide, acetophenone and benzophenone. From the carbon tetrachloride and the benzene (and possibly from other solvents) the solid polymer was obtained again as the solvent evaporated.

Combustion analyses of this polymer gave for lot (1), %H = 6.67 and %C = 79.75, and for lot (2), %H = 6.71 and %C = 80.0; while the calculated values from the formula $(C_8H_8O)_n$ are %H = 6.72 and %C = 80.0.

The molecular weight of the polymer was found from cryoscopic measurements. In solution in bromoform the depression of the freezing-point for a solution of 1 gram of polymer in 100 grams of solvent was 0.1895°, and the molecular weight = 144/0.1895 = 760; whence n is 6. (The molecular weight of $(C_8H_8O)_n$ is 120.n) But compounds like $(C_8H_8O, CHBr_3)_2$, M.W. = 746, are possible. In carefully purified benzene the depression of freezing point for a solution of one gram of polymer in 100 grams of solvent was 0.142°; whence the molecular weight was 51/0.142 = 359; and thus n is 3. (Raoult's cryoscopic constant for benzene is quoted from 49 to 52, and we suppose that similar or larger errors are probable for the 'Raoult's constant' given for the other liquids used.) In ethylene dibromide (K = 118) the molecular weight of the polymer was 383; in benzophenone (M.P. = 47° and K = 98) the molecular weight was 400 approximately; in acetophenone (K = 56.5) the molecular weight was 349; in cyclohexanol (K = 383) the molecular weight was 330; and in paraldehyde (K = 70.5) the molecular weight was 403. Thus in the last six solvents the polymer dissolved as $(C_8H_8O)_3$ and in bromoform as $(C_8H_8O)_6$. The crystal unit of the solid polymer is therefore $(C_8H_8O)_{3n}$.

Summary

1. Phenylacetaldehyde polymerises with time.

2. Any sample becomes with age more viscous, denser, and of higher refractive index, until finally there separate crystals of the polymer. The density and the refractive index increase, in general, linearly with the time, but the viscosity increases much more rapidly.

3. The refractive index is a very convenient property by which to determine the age of a specimen of phenylacetaldehyde.

4. Phenylacetaldehyde does not oxidise appreciably in air at ordinary temperatures.

5. In most solvents the polymer dissolves as $(C_8H_8O)_3$, but in bromoform as $(C_8H_8O)_6$.

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NEW BOOKS

An Introduction to Chemistry. *By John A. Timm. 20 × 14 cm; xviii + 561. New York and London: McGraw-Hill Book Company, 1930. Price: $3.50.* In the foreword John Johnston says: "Since the war, and probably by reason of the emphasis then placed upon chemical knowledge, there has been a growing dissatisfaction with the kind of introductory course in chemistry commonly given in college, particularly when this is the only chemistry course taken by many of the students. Believing in the desirability of a discipline planned specifically for the considerable group of students who will take no other course in physical science, the Faculty of Yale College about four years ago inaugurated such a course, which, since its inception, has been taught each year to a larger number of students; and the present book is the outcome.

"The general purpose is to give the student some acquaintance with the subject as a whole—with the general philosophy of physical science and with its manifold bearing upon the life of each one of us. The syllabus is based on a belief in the cultural value of the philosophy of a subject as compared with that of mere information, and hence it aims to emphasize that what we are dealing with is a series of related phenomena rather than a host of separate facts. In other words, this course endeavors, not to give the student a temporary command of assorted facts, relating to restricted classes of substances, but to correlate and to explain in simpler terms, some of the chemical and physical phenomena which he encounters every day. The subject of chemistry is regarded as a living tree, with roots becoming always better established and with new branches appearing and growing, rather than as a finished array of ordered facts; for much more remains to be discovered than is now known, and the process of discovery is as romantic and as joyful as is the exploration of any new region.

"It was intended that the range of topics discussed would be limited to those which can, in the time available, be treated thoroughly; that every effort would be made to interest the student by reference to familiar things for instance, to the automobile, which illustrates a great variety of chemical processes and physical phenomena; and that there would be considerable collateral reading of good biographies of scientists and of other books dealing generally with physical science," p. xiv.

The scope of the book is shown by the titles of the chapters: introduction; the nature of matter; the nature of gases; the nature of liquids and solids; changes of state; molecules; atoms; the shorthand of chemistry; the nature of chemical reactions; rate of chemical reactions; the atmosphere; the nature of combustion; our fuel resources; the metals; iron and steel; the periodic law; sub-atomic phenomena; the structure of the atom; the planetary electrons; radioactivity; the nature of energy; the nature of heat; radiation; the complete spectrum; the emission and absorption of radiant energy; water; solutions; alloys; electrolytic dissociation; electrolytes; reactions of electrolytes; the acid heavy chemicals; the basic heavy chemicals; electrolysis and the electrochemical industries; electrochemical cells; colloids; plant food; organic chemistry; carbohydrates, fats, and proteins; coal tar.

"In Chap. VIII you were introduced to chemical shorthand; to the mysteries of chemical symbols and formulae. You will now be introduced to a more complex form of chemical shorthand—the chemical equation. You have probably heard of this instrument of intellectual torture before from others who have struggled with elementary chemistry; but do not become unduly alarmed for we shall consider it here as a great convenience, the meaning of which you must understand, but shall not subject you to a drill in writing them for the purpose of giving you facility in their use. Such a drill is necessary in the training of a chemist as he must be able to handle the tools of his profession but it is neither necessary nor desirable that your time be wasted in this way," p. 87.

"Not all of the effects of ultraviolet light are harmful, however. Too much of a good thing is always bad. Rickets has always been a distressing disease of childhood. It is a defect in the mechanism by which the body controls the development of bone. Children with rickets suffer from a delayed and abnormal bone development which results in a warpage of the body contours. The teeth also are affected. It is a disease of the temperate zones only. Practically no cases are known in the arctic and tropical climates. It has been suspected for at least a few hundred years that sunlight was a preventive. Children who live in tropical climates wear little if any clothing and hence escape rickets. In the temperate zone, however, during the long winter months children are kept indoors most of the time and so are screened by window glass from the ultraviolet light of the sun. Also these are the relatively dark months of the year, hence rickets develops almost exclusively in the winter time. A striking illustration of the efficacy of sunlight in preventing this disease was brought out by Hutchinson and Shole in their study of rickets among the children of India. The children of the laboring class which run naked in the streets never develop rickets but those of the high-caste Hindus generally develop severe cases because of the fact that their mothers must be kept in seclusion due to the religious custom of purdah. This naturally results in the children being kept in dark rooms with their mothers," p. 293. One rather wishes that the author had mentioned why people do not have rickets in the polar regions. While he did not wish to discuss vitamines then, a reference to food would have been helpful.

The paragraph on p. 309 indicates Einstein as a guesser and not an accumulator. "In 1905 Einstein enlarged this theory. He proposed the theory that not only do atoms absorb and emit light in fixed finite quantities but also that these quanta of radiant energy preserve their identity as they travel through space. At the time he had little proof as to the truth of his proposal but he expected that in time evidence would accumulate to prove its correctness. This has been the case,".

"When we look more closely into the nature of the organic compounds of which plants are composed to discover why these elements are essential, we find that most of these can be divided into three classes; the carbohydrates, which class includes the sugars, starches, and cellulose; the fats; and the proteins. Carbohydrates and fats are compounds of carbon, hydrogen, and oxygen, and the proteins in addition to these three elements contain nitrogen and sulfur. Certain compounds within the nuclei of the plant cells contain phosphorus; and that most important compound, chlorophyl, the green coloring matter in the leaves which serves as the link by which the radiant energy of the sun is made available to all living organisms, contains magnesium. Potassium is indubitably essential to plants, and yet it does not appear in the molecules of the organic compounds of which they are composed. It seems to aid in some way in the synthesis of the starches and sugars and helps to keep up the vigor of the plant, making it more resistant to disease. The need of iron is in some way connected with the synthesis of chlorophyl, and calcium, in a manner that is little understood, aids in the formation of the cell-wall material, or woody fibre," p. 486.

"Ethylene is now used extensively to color green oranges and lemons. Citrus fruit becomes ripe before its skin loses the green color. It can be shipped in this condition with little danger of spoilage and then brought to full color by ethylene gas after it has arrived at its destination. In as low a concentration as one part of ethylene per 3,000 parts of air, 25 cu. ft. of this gas can color a carload of oranges in 5 days. Ethylene is also used as a general anaesthetic in medicine. The story of the discovery of its use for this purpose is interesting. About 1908 a Chicago florist discovered that several shipments of carnations promptly closed up their petals and went to sleep when placed in a certain corner of his greenhouse. He called Dr. Crocker, a botanist in the University of Chicago, into consultation. The latter discovered that a leaky gas pipe was doing the damage. Since illuminating gas is a mixture of various substances (p. 141), he tried the action of each of these on carnations and found ethylene to be the offender. Finally, in 1922, Professor Luckhardt, also of the University of Chicago, with the aid of Mr. Carter, found that rats in an atmosphere of 80 per cent ethylene curled up and went to sleep and in this way its anaesthetic properties were discovered," p. 507.

"In 1909 Friedländer succeeded in establishing the structure of Tyrian purple and, oddly enough, found out that it had already been synthesized five years before by Sachs but had been rejected as an inferior dyestuff! It was a dibrom-indigo," p. 542.

The reviewer would have liked to have seen one chapter on qualitative and quantitative analysis and one on medicine. The first would be easy to write and the second difficult. There are some things which should be changed in the second edition. The statement of the generalized gas equation, p. 25, is right but nobody will recognize it. It would be better to connect it with the form PV = RT. On p. 46 it would be better to give the normal boiling, in Ecuador or on Pike's Peak, rather than to say that it is lower than at sea-level. There is nothing to show the magnitude of the change and that is what one is interested in. The reviewer may be wrong; but he thinks that helium has been liquefied at the Bureau of Standards, p. 54. On p. 56 the word "liquefier" is spelled wrongly in the diagram. The reviewer does not like the spelling of "liquidous" and "solidous", p. 354.

On p. 124 we read that resuscitation from carbon monoxide poisoning "involves the administration of a mixture of 95 percent oxygen and 5 percent carbon dioxide to the victim. The carbon dioxide is needed to stimulate respiration as experiments by Yandell Henderson of Yale have shown." One would like to know why carbon dioxide is needed to stimulate respiration. The reviewer feels that it would be better to start with the flames containing incandescent solids rather than with the statement, p. 129, that "a flame is produced whenever an exothermic reaction between gases takes place so rapidly that they become luminous." Nothing is said about wood-fires, candles, oil lamps, acetylene burners, or magnesium flash-lights.

The reviewer questions the wisdom of saying, p. 337, that sugar lowers the vapor pressure of water because it decreases the surface concentration of water. If that were true, we should get different vapor pressure relations for solutes which raised or lowered the surface tension and there is no experimental evidence for this as-yet. Also, this point of view is absolutely inconsistent with the behavior of three-component systems.

As is apparently inevitable nowadays, there is a good deal of careless proof reading. The author is probably responsible for writing Sir Humphry Davy's Christian name as Humphrey.

We had hoped to put in a course in pandemic chemistry at Cornell; but conditions were not favorable, and Yale is the first of the larger universities to do so. Apparently it has been a success there, as it ought to be. Last year there were two hundred and fifty students taking it, and this text was written for their benefit. It should also make possible the giving of similar, much-needed, courses elsewhere.

The principle involved has been discussed unfavorably by McPherson in his presidential address before the American Chemical Society, published in Science. This was before he had seen Timm's text. "There has been much discussion as to whether chemistry viewed in this way as a constituent of the course in liberal arts should not have a different treatment from the course arranged for our future chemists. We have, at least, a name [pandemic] for such a course; but, in the main, the discussions have had little influence on the character of the course.

"Two methods of procedure are open to us. (1) We may separate our students into two classes, according to whether or not they expect to make chemistry their life work, and give to each class courses differing fundamentally in character; or (2) we may so shape our introductory course that it will serve the aims of education and be of value to all students alike. The first of these methods is open to the very serious objection that the course offered to the general student is likely to resolve itself into a collection of facts pertaining to chemistry, interesting undoubtedly, but serving neither the aims of education nor those of science—enjoyable bed-time reading but out of place in serious college work. Equally true, the technical course might miss many of the suggested and cultural values. It would seem entirely possible to frame a course that would be of value to all alike, providing a foundation knowledge of the science of chemistry but stressing acquaintance with fundamental laws and principles; also habits of clear thinking and independent judgment such as contribute to constructive ability and ultimately to good living as well. Many a liberal arts student, not supposing himself interested in science, through such a course has had awakened the profound intellectual passion of his life."

By a suitable juggling of the premises one can arrive at any desired conclusion. McPherson slips in the phrase about making chemistry their life work and thereby shunts the prospective engineers, medical men, and biologists into the pandemic course, which nobody else has suggested doing. While a pandemic course might conceivably be a collection of bed-time stories, no one could classify Timm's text under that head, nor that of Findlay. McPherson ignores the question whether a course which leads up to analytical chemistry, organic chemistry, physical chemistry, etc., can possibly cover the ground which should be covered by the pandemic course. Having eliminated arbitrarily the good points of one and the weak points of the other, McPherson concludes triumphantly that there is no room for two courses. His conclusion will not be accepted by anybody who has given any careful thought to the subject. *Wilder D. Bancroft*

Band Spectra and Molecular Structure. *By R. de L. Kronig. 22 × 14 cm; pp. x + 163. New York: The Macmillan Company; Cambridge: The University Press; 1930. Price: $3.50; 10 shillings, 6 pence.* This book takes its origin in a course of lectures given at Cambridge about eighteen months ago. It is scarcely necessary therefore to add that it is an accurate and authoritative presentation of the subject on its theoretical side. Prof. Kronig has himself made notable contributions to this subject and we are indebted to him for the present excellent little book. It is essentially concerned with the theoretical developments: specific spectra and experimental matters are not dealt with. The reader is plunged without delay into the application of wave mechanics to the diatomic molecule: a knowledge of the necessary mathematical technique is assumed. The major problems of the electronic, vibrational, and rotational energy levels are dealt with in this fashion. In the next chapter the more detailed problems of multiplet structure and fine structure generally are treated by the perturbation methods of quantum mechanics. A further chapter deals with selection rules and intensities in diatomic molecules: it is a particularly good summary of these and kindred matters. Under the heading of Macroscopic Properties of Molecular Gases the author has touched on light-scattering, dispersion, the Kerr and Faraday effects, dielectric constants, magnetic susceptibilities and specific heats. Finally there is a short chapter on the problems of molecule formation and chemical binding. There is a valuable bibliography of over three hundred and fifty papers grouped appropriately under the above headings: this very greatly enriches the book.

To the mathematical physicist and those interested in the diverse fields of application of the new quantum theory the book can be highly commended. It brings together a great variety of information, otherwise scattered too widely through the Journals of Learned Societies and other publications. We imagine however that the book may be found difficult in large part by those without considerable mathematical equipment. *R. C. Johnson*

Photochemistry. *By D. W. G. Style. 18 × 11 cm; pp. vii + 96. London: Methuen and Co., 1930. Price: 2 shillings, 6 pence.* Dr. Style's little book on Photochemistry provides a welcome introduction to a branch of physical chemistry which of recent years has undergone a very extensive development. This development is one of general importance and interest, and a book of this nature should therefore appeal to a wide circle of readers. This is particularly the case in the present instance, since while the principal results and conceptions of photochemistry, such as the law of photochemical equivalence, or chain reaction mechanism, are clear cut and well-defined, the large amount of work which has gone to their establishment is detailed and technical. It involves a close quantitative study of a large number of photochemical reactions and their critical comparison with the results of spectroscopic study; and while the more specialised student has been catered for by at least two admirable text-books in the English language, the general reader has probably up to the present found it difficult to assimilate the fundamental facts and principles without an undue amount of labour.

To this end, Dr. Style's book is of great assistance; it aims at giving a concise account of the main aspects of photochemistry without a burdensome amount of detail, and altogether forms a well-balanced whole. At the same time the author has been at pains to introduce the reader to the spirit of the subject by discussing in some detail a limited number of well-chosen examples.

The introductory chapter deals in main with the subject of light absorption, brief reference being made to the quantum theory of band spectra and its bearing on photochemical processes. This is somewhat further developed in the second chapter, which discusses the nature of the primary photochemical change effected in the molecule. In Chapter III the secondary "dark" reactions which follow the primary processes of molecular dissociation or activation are considered, and it is shown how the varying types of photochemical change may ge generalised by the conception of the reaction chain. Many of the concepts of Chapters II and III are developed in greater detail in the fourth chapter, which deals with the dependence of quantum yield on temperature and wave-length. The book closes with a short chapter on experimental methods. There are a short bibliography, a table of references, and an index.

The reviewer can only express his admiration at the large amount of useful information that has been collected in a small space, and can recommend this little work to those interested as a representative taste of a very interesting subject.

R. G. W. Norrish

Recent Advances in Physical and Inorganic Chemistry. *By Alfred W. Stewart. 22 × 14 cm; pp. x + 387. London: Longmans, Green and Co., 1930. Price: 18 shillings.* The fact that this is the sixth edition of this book is sufficient testimony that the author is able successfully to summarise the more important advances made in chemistry in a way which appeals not only to the aspirant for an honours degree, but also to those who desire to keep in touch with the trend of modern work.

In the present volume, which contains seventy-five more pages than its predecessor, the author's main topics consist of the advances made in our knowledge of spectra—including line, X-ray, positive-ray, band, emission and Tesla-luminescence spectra—and of radio-activity. Subjects arising from these, as, for example, the structure of the atom, isotopes, isobares, the discovery of hafnium, etc., are given due consideration. In addition, there are given chapters dealing with the various hydrides of metals and non-metals, which have assumed theoretical importance in recent years, with certain flame reactions and with the Donnan equilibrium.

Generally speaking, the subject matter is right up-to-date, but in the chapter on the Donnan equilibrium, which deals with a subject which seems to be somewhat alien to the rest of the book, the latest reference to gelatin is dated 1918.

The author is neither so outspoken in his antipathies nor so dogmatic in his statements as he has been at times in former editions, and the present volume is well worth the study of those who desire a readable and corrected account of recent advances.

T. Slater Price

Messungen elektromotorischer Kräfte galvanischer Ketten mit wässerigen Elektrolyten. *By Carl Drucker. 24 × 17 cm; pp. xx + 234. Berlin: Verlag Chemie, 1929. Price: 24 marks.* This is No. 10 of the *Abhandlungen der deutschen Bunsengesellschaft* and is a supplementary volume to No. 5. It contains chiefly data which appeared from 1914 to 1927 both inclusive. Cells in which non-electrolytes have been added are also included. The book is invaluable for reference purposes.

Wilder D. Bancroft.

THE COLLOID CHEMISTRY OF THE NERVOUS SYSTEMS. I*

Sodium Thiocyanate Therapy. I

BY WILDER D. BANCROFT AND J. E. RUTZLER, JR.**

Fifty-six years after his work was published we find Bancroft and Richter[1] honoring the great physiologist and prophet, Claude Bernard, by showing that his theory of anesthesia[2] explains correctly the facts that are met with in the process of the loss of consciousness by the agencies of man. We find further tribute to Bernard's far-sightedness when we consider the fact that his works were first published[3] only five years after Graham differentiated colloidal suspensions from true solutions by means of his famous dialyzer.

The theory of anesthesia having been definitely settled, it can become more solidly intrenched in direct proportion to its ability to serve as a basis for accurate and sweeping prediction as to the effect that various chemicals will have upon animals under anesthetics. In other words, how often can one predict accurately the effect of adding drug B to an animal under the influence of anesthetic A?

The thesis of this paper is, then, to show how, with Claude Bernard's theory of anesthesia as developed by Bancroft and Richter as a basis, the state of anesthesia is affected by certain chemicals, particularly sodium thiocyanate. As the story unfolds, we will consider sodium thiocyanate in its relation to narcoses by means of ether, "amytal," morphine, "nembutal," and alcohol. Then, using the same type of theoretical considerations, the effect of sodium thiocyanate upon the action of histamine, strychnine, and anaphylactic shock will be described and explained.

In order to start with a clear idea of the phenomenon of anesthesia we will first quote the Claude Bernard theory as put forth by Bancroft and Richter: "If the colloids of a cell are reversibly coagulated (anesthesia will result, if the cells are those of the sensory nerves) and the agent (the anesthetic) that caused the flocculation is displaced by a substance of weaker flocculation capacity for the given concentration, naturally the bio-colloids are peptized again by the electrolytes. Concurrent with this peptization there will be a return of irritability and consciousness. Now (in the normal case of a person recovering from an anesthetic) the agents that are responsible for the peptization are the electrolytes within the cells." This, briefly, is the theory of anesthesia as it stands today.

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*This work is part of the programme now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research, established at Cornell University by August Heckscher.

**Eli Lilly Research Fellow.

[1] J. Phys. Chem., 35, 215 (1931).

[2] "Leçons sur les anesthésiques et sur l'asphyxie" (1875).

[3] "L'Anesthésie," Union med., Paris, 8, 109 (1867).

The authors say, in another part of their paper: "Consider the simplest possible theoretical case, in which the drug is affecting only one substrate. The possible methods of elimination of the drug have already been discussed in the paragraph on recovery; suppose that these methods of elimination are slow and we desire to hasten it. Another substance is given which will be adsorbed upon the same substrate and displace some or all of the original material, thus increasing its effective concentration so that it may undergo the reactions of detoxication faster or diffuse out more rapidly. This method is very effective, provided that the antagonist does not complicate the situation by its own action. It can be seen that the drug has been displaced by another whose physiological action is less but whose adsorption is greater. The extent of the adsorption is determined by the concentration, so there will be antagonizing concentrations below which this effect will be very small Also if the elimination of the drug is not hastened by the displacement the effect of the antagonist will only be transient."

In another paper Bancroft and Richter[1] draw the following conclusions:

"1. Claude Bernard was right in postulating that reversible coagulation of the colloids of the sensory nerves produces or accompanies anesthesia.

"2. Decreasing stability of the nerve colloids means increasing irritability up to the point of incipient coagulation.

"3. Claude Bernard's theory affords an apparently adequate explanation of the difference between a general and local anesthetic.

"4. Claude Bernard's theory accounts for the effects observed when morphine is used together with chloroform or ether.

"5. Claude Bernard's theory offers an apparently adequate explanation for the difference between a true anesthetic and a habit-forming drug.

"6. Claude Bernard's theory accounts for the phenomena observed in the action of mercuric chloride on bacteria, of strychnine on frogs and dogs, and of hydrocyanic acid on the eggs of citrus scale.

"7. Decreasing stability of a suitable colloid or group of colloids—accompanied by increasing irritability up to a certain point—and then reversible coagulation will apparently account for the law, accepted as universal by biologists, physiologists, and bacteriologists, that all depressor substances exert a stimulating effect when used at an appropriate dilution.

"8. Claude Bernard's theory offers a clue to a scientific method of counteracting habit-forming drugs.

"9. Nitrous oxide and acetylene are not true anesthetics in the sense that ether and chloroform are. These two gases cause reversible coagulations of the colloids of the sensory nerves indirectly, and not directly as ether and chloroform do.

"10. Claude Bernard's theory dealt with the colloids of sensory nerves. There is, therefore, nothing to prevent reversible coagulation of other materials besides proteins from being important in connection with anesthesia. It seems wise, however, to see how much can be explained solely by reversible coagulation of the proteins. We then have the behavior of the other colloids in reserve to be called into play when and as needed.

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[1] Proc. Nat. Acad. Sci., 16, 573 (1930).

"11. The Overton-Meyer theory accounts satisfactorily for many, though not for all, cases of cell permeability; but it is not true that all substances which enter the cells produce narcosis, and consequently the Overton-Meyer theory is a theory of permeability and not in any proper sense a theory of narcosis at all."

These considerations, then, form the basis of the work reported in this paper.

In the same paper the authors postulated tentatively that the colloids of the sensory nerves are albumin-like in nature. This immediately gives us a foothold; for it becomes obvious that here also the lyotropic series of the anions must play a dominant role. Höber[1] and also Pauli[2] have shown that albumin on the alkaline side of an $(H^+) = 1 \times 10^{-7}$ is peptized by anions in the order $CNS > I > Br > NO_3 > Cl > CH_3COO$; the sulphate, tartrate, and citrate ions[3] can be added in that order to make the series more complete. At the same time the order of the cations is[4] $Cs > Rb > K > Na > Li$. So long as one does not work with living things, it does not make any vital difference which one of the alkali metal cations is used; the cations having higher valences tend to precipitate natural egg albumin. Upon making a natural egg albumin sol acid, it becomes charged positively,[5] then both of the ion series are completely reversed; the ions that peptize the negatively charged albumin the most effectively now coagulate it most strongly.

Now, the sensory-nerve colloids, if they are albumin-like, or less hydrophilic and globulin-like, should adsorb the thiocyanate ion strongly and as a result become peptized and more finely dispersed. We know that coagulated egg white can be peptized by the thiocyanate ion.[6] The next two steps immediately become obvious; first we must choose a cation to go with the thiocyanate radical, and then apply the compound chosen to the peptization of reversibly-coagulated sensory-nerve proteins, thus bringing animals out of anesthesia.

For the cation, chemical considerations and the lyotropic series tell us that we are limited to those that will give us a respectably soluble salt and one that will not interfere with the peptizing action of the thiocyanate ion. This leads to the choice of one of the alkali metals. The natural choice, then, lies between potassium and sodium. Some care must be exercised in deciding whether to use sodium or potassium thiocyanate in living things to peptize reversibly coagulated colloids. Lusanna[7] found, on studying the effects of different metal chlorides upon frog muscle in faradic excitation, that lithium does not affect the contractility, but depresses respiration; potassium destroys the contractility but does not affect respiration; and sodium affects neither the contractility nor the respiration.

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[1] Hofmeister's Beitr., **11**, 35 (1907).

[2] Hofmeister's Beitr., 5, 27 1903; Biochem. Z., **47**, 269 (1912).

[3] Freundlich: "Colloid and Capillary Chemistry" (1922).

[4] See also, Robertson: "Physical Chemistry of the Proteins," 120 (1918).

[5] Hardy: J. Physiol. **24**, 288 (1899).

[6] Bancroft and Rutzler: J. Phys. Chem., **35**, 144 (1931).

[7] Bull. Soc. Med., No. 4 (1907).

Gellhorn[1] showed that potassium contraction in both smooth and striated muscle is favored most by the thiocyanate ion; the order of the ions in this respect is $SO_4 > Cl > Br > I > CNS$. Menten,[2] working on the sciatic nerves from the brachial plexus supplying the fore-paws in dogs, found that, with the exception of potassium citrate, acetate, oxalate, and tartrate, many salts of potassium produce a loss of irritability. He states that the salts of sodium do not have this anesthetic effect.

Potassium contracts voluntary muscles,[3] whereas sodium does not exhibit this effect. Potassium is a powerful cardiac poison,[4] rubidium and caesium act the same way, but to a much less extent. Spiegel[5] says: "Therefore, contrary to the original formulation of Blake, but in accordance with the demands of the periodic system, potassium shows properties in common with the other alkali metals (excepting sodium)."

Kahn[6] has studied the effect of injections of various amounts of potassium thiocyanate (which was cyanide free) into the dorsal lymph sacs of frogs. Depending upon the dose of potassium thiocyanate used, he found that the heart was stopped in systole, and violent strychnine convulsions, tetanic contractions, opisthotonus, and hypersensitiveness occurred. Doses up to 0.24 milligrams per gram resulted in the survival of the frog, whereas a dose of 0.35 milligrams per gram was lethal. Somewhere in between one would expect to find the M. L. D. (minimum lethal dose). Kahn then worked with guinea pigs and observed that here again the potassium thiocyanate caused violent tetanic convulsions. The dose that the guinea pig could stand was somewhat less than the M. L. D. for frogs. In conclusion Kahn says: "Potassium sulphocyanate is toxic to both plants and animals. Its toxicity is so marked that indiscriminate dispensation of the substance to patients is dangerous."

There is food for thought in the fact that a completely non-toxic substance has been prepared[7] that consists of thiocyanate adsorbed upon albumin; it is called "rhodalzid."

So much for the potassium salt, as it is evidently distinctly toxic to animal life. We are thus forced to choose sodium thiocyanate as the compound most likely to peptize efficiently the reversibly-coagulated colloids of the sensory nervous system under the influence of an anesthetic. One objection that might be raised thoughtlessly to the use of sodium thiocyanate is that in the body it might be converted into cyanides. There are several reasons why this possible objection should be overthrown immediately; in the first place the thiocyanates are chemically more stable than the cyanides; in the presence of sulphur or oxygen, cyanides tend to go to thiocyanates and cyanates respectively upon the least provocation. Secondly,[1] "the cyanide of potassium is liable, during putrefaction, to be converted into sulphocyanide (KCNS)." Taylor continues: "A case of poisoning occurred to Dr. Letheby in September, 1864, in which sulphocyanide of potassium and carbonate of potash were found in the stomach in place of the poison actually taken." The potassium atom, of course, plays no significant part in these changes, so that the same reactions would hold for sodium thiocyanate. Thirdly, Grober[2] found that feeding small quantities of prussic acid increased the output of potassium thiocyanate. So it seems probable that cyanides go to thiocyanates in the body. McGuigan,[3] Bodansky,[4] and Franz[5] dispose of all doubt concerning the possibility that thiocyanates go to cyanides in the body; they all say either that cyanides go to thiocyanates in the body, or else that cyanides are not formed from thiocyanates *in vivo*.

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[1] Archiv ges. Physiol. (Pflüger's), 219, 761 (1928).

[2] Am. J. Physiol., 31, No. 2, 85 (1913).

[3] Spiegel: "Chemical Constitution and Physiological Action," 27 (1915).

[4] Astolfoni: Archiv intern. Pharmacodyn., 11, 381 (1903).

[5] "Chemical Constitution and Physiological Action," 27 (1915).

[6] "Biochemical Studies of Sulphocyanates," Columbia University Dissertation, 74 (1912).

[7] Diena: Biochem. Z., 39, 13 (1912).

Experimental Study

1. Ether

A young rabbit weighing approximately 600 grams was selected for this work. The bottom of a 500 cc. beaker was covered with cotton; ten cc. of peroxide-free ether was poured on the cotton, and the beaker placed tightly over the head of the rabbit. At first the animal struggled violently; this was the well-known excitatory stage during which the sensory-nerve colloids are on the verge of reversible coagulation. The administration of the anesthetic was continued until the lid reflex disappeared. This corresponds to a very deep anesthesia, for Gwathmey[6] states that the lid reflex is weakly present in surgical anesthesia. It took three minutes 20 seconds to reach this stage, as timed by a stop-watch. Four and one-half minutes after the mask was removed there was a slight lid reflex; the animal was completely out of the anesthesia six and one half minutes after the administration was stopped. This return to normal was judged by the fact that the rabbit sat up of its own accord. The excitatory stage upon recovery was not pronounced.

The animal was then allowed several hours in which to come back completely to normal, although no abnormal symptoms were noticed after it arose from the narcosis. Then it was again anesthetized exactly as before (body position and everything being the same) except that the anesthetic was administered for a period of four minutes ten seconds. During the last minute that the ether was given, 0.9 cc. of a 10% solution of sodium thiocyanate was injected into the marginal vein of the ear. As before, the lid reflex disappeared in three minutes 20 seconds. Thus, the period of administration of the anesthetic was 25% longer in the experiment where the sodium thiocyanate was given. The lid reflex this time returned 50 seconds after the mask was removed, or 540% more rapidly. The animal arose of its own accord four and one-half minutes after the mask was removed, or 44% faster. Although the animal arose of its own accord, it was very intoxicated. The intoxication wore off quickly. Thus, in this case, the period of irritability upon recovery was considerably more marked. Apart from the gross action of the thiocyanate ion, which was to repeptize the reversibly-ether-coagulated sensory-nerve proteins, what does the quicker recovery and resultant intoxication mean?

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[1] Taylor: "A Treatise on Poisons," 601 (1875).
[2] Deutsch. Archiv Clin. Med., **69**, 243 (1901).
[3] "A Textbook of Pharmacology and Therapeutics," 102 (1928).
[4] J. Pharmacol., **37**, 463 (1929).
[5] J. Chem. Soc., **102** II, 668 (1912).
[6] "Anesthesia," 194 (1914).

It merely means that both the ether and the thiocyanate ion were courting the sensory nerve colloids. Obviously the thiocyanate ion won, but not without a struggle; for the observed period of intoxication was the excitation upon recovery during which time the presence of the ether with its coagulating effect prevented the thiocyanate ion from restoring the nerve colloids of the rabbit completely to normal. Had the animal waked up the second time in six and one half minutes (a condition obviously impossible of fulfillment) there would have been no intoxication. The intoxication (excitation) was, therefore, a natural consequence of the treatment.

The next question that might be brought up is, why did the lid reflex return 540% faster with the help of sodium thiocyanate, while it caused the rabbit to arise only 44% faster?

Here again the answer is not difficult. The rate of adsorption is greater just after adsorption starts than it is after it has been in progress for some time. So, the greatest evident peptizing effect is at the start, and as time progresses the adsorption makes itself much less evident. Suppose we take a cloudy egg albumin sol. Upon adding a solution of sodium thiocyanate to this we see an immediate and large decrease in the degree of turbidity but certainly all of the thiocyanate ion that can be adsorbed is not adsorbed immediately. Still the amount that the sol clears up in the next few hours is almost imperceptible.

One might say that in this experiment the rabbit was shocked out of the anesthesia by the injection. There is no trouble encountered in refuting this argument; it should be remembered that the injection was made while the ether was being administered. Animals can stand the severe shock of surgery, so there is no evident reason why they should be bothered by the mere injection of a small amount of sodium thiocyanate. Cases are on record[1] in which 1,000 to 2,000 cc. of "normal saline solution" were injected intravenously into patients under oil-ether colonic anesthesia without any mention being made of their having been roused from the narcosis. So, the shock objection is overruled.

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[1] Gwathmey: "Anesthesia," 462, 463 (1914).

In the case of ether anesthesia the respiratory center in the brain is only slightly affected in comparison to other centers.[1] The importance of this will become evident as this paper progresses.

Concerning the toxicity of the sodium thiocyanate, it is interesting to note that in this case the dose of salt was equivalent to 150 milligrams per kilogram, whereas Kahn[2] found that potassium thiocyanate in a dose of 150 milligrams per kilogram is fatal to guinea pigs. Thus, a dose at least equal to the dose of potassium thiocyanate can be used with impunity when one employs the sodium salt.

It is almost a shame to perform such an experiment as that which we have described, for, granting a normal animal and a careful technique, the case is so clear-cut that the experiment almost assuredly could have done naught but succeed.

2. "Amytal"

Ether being easily and quickly eliminated, and requiring a high concentration[3] (150 milligrams per 100 cc. of blood immediately after cessation of the inhalation) to be effective, is not very strongly adsorbed by the sensory nerve colloids. For that reason the task of displacement and subsequent peptization to which the thiocyanate ion was assigned was not a very difficult one.

In casting about for an anesthetic capable of exerting the thiocyanate ion into a demonstration of its efficacy it was decided that there are several reasons why "Amytal" (iso-amylethyl barbituric acid, the sodium salt is used in anesthesia) should be such. Reference to a paper by Clowes[4] on anesthesia by means of sodium "amytal" brings forth several facts. "Amytal," being a solid, is not eliminated through the lungs; small doses, 40 to 50 milligrams per kilogram injected intravenously into dogs, bring about a deep narcosis. The compound is not eliminated quickly, for one of its chief disadvantages as an anesthetic is that "following anesthesia (deep surgical anesthesia lasts for a period of one to three hours) there is a somewhat prolonged period of post-operative sleep." Thus, it may be safely assumed that "amytal" is, compared to ether, very strongly adsorbed by the sensory nerve colloids. This, of course, results in their reversible coagulation. It would be a boon to the general use of "amytal" for the induction of anesthesia if the post-anesthetic sleep could be "antidoted" by other means than by the use of ephedrine sulphate and caffeine sodium benzoate.

A solution of 0.03 grams of the acid "amytal" was prepared by gently warming it in distilled water[5] and slowly and carefully adding sodium carbonate until the "amytal" was completely dissolved. Following the method of Clowes, this solution was injected slowly into the marginal vein of the ear of a young rabbit weighing about 600 grams. Before the injection was completed the animal was entirely limp and the lid reflex had disappeared. This rabbit was used as the control. Thirty-nine minutes after the "amytal" was administered, a hypodermic needle was thrust gently under the skin; the rabbit showed no signs of feeling this. The respiration was only 14 per minute after 42 minutes; it was 18 per minute after one hour 16 minutes. This shows that the colloids of the respiratory center were affected by the anesthetic. Two hours after the anesthetic was given there was no sign that the lid reflex had returned; the animal was still unconscious 14 minutes later. In two hours 20 minutes there was a very weak lid reflex; eight minutes later the rabbit began to stir; consciousness was fast returning. One minute later the animal was definitely conscious, but could not sit up; it was still unable to sit up after three hours 14 minutes. The rabbit was up and about four hours 14 minutes after the induction of anesthesia. It showed no desire to eat at this time.

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[1] Crile: "A Bipolar Theory of Living Processes," 101 (1926).

[2] "Biochemical Studies of Sulphocyanates," Columbia University Dissertation, 76 (1912).

[3] Gwathmey: "Anesthesia," 196 (1914).

[4] Clowes et al: Proc. Soc. Exp. Biol. Med., **26**, 399 (1929).

[5] The authors wish to thank Dr. G. H. A. Clowes of Eli Lilly and Co. for generously supplying them with sodium "amytal."

At the same time a litter-mate of the rabbit described in the above experiment (weight the same) was anesthetized in an identical manner with the same compound. However, instead of allowing the animal to sleep peacefully, four minutes after the "amytal" was administered, 1 cc. of a 10% solution of sodium thiocyanate was injected intravenously, using the marginal vein of the ear. The injection was made slowly; and the rabbit raised its head and worked its legs before it was finished. Fifteen minutes later the lid reflex had returned definitely; this was 19 minutes after the anesthetic was injected. When 25 minutes had elapsed 0.5 cc. of the same sodium thiocyanate solution was injected subcutaneously. During the injection the rabbit struggled. very hard to arise, and it very distinctly felt the needle when it was inserted. It will be remembered that the control rabbit exhibited no response to the insertion of the needle under the skin. When the injection was completed, the animal arose of its own accord, and there was a very strong lid reflex. This phenomenon was followed quite shortly by a relapse of strength which was, however, not accompanied by the loss of the lid reflex. The respiration was 32 per minute after 33 minutes of the narcosis, as compared to a respiration rate of 14 per minute in the control after 42 minutes of the narcosis. This is striking, for the rate of respiration in the case where the sodium thiocyanate was used was practically 130% greater. Fifty-eight minutes after the "amytal" was given 0.5 cc. more of the sodium thiocyanate solution were injected subcutaneously. The effect of this second subcutaneous injection was the same as the first time it was done; only it was much more striking, and the rabbit so far as one could judge largely overthrew the effects of the anesthetic. The animal had a great deal of strength after this injection; there was not a noticeable relapse of any kind from this time on. Meanwhile the control rabbit slept on without even a sign of the return of the lid reflex. The respiration rate was 35 per minute after one hour seven minutes. When one hour 42 minutes had elapsed 0.2 cc. more of the thiocyanate solution was injected subcutaneously; this induced the animal to crawl around, although it was still somewhat weak. The hind legs were not completely normal, because the rabbit walked rather than hopped. So, after one hour 53 minutes, 0.3 cc. more of the sodium thiocyanate solution was introduced by the subcutaneous route. This caused the hind legs to become normal, and the rabbit hopped five or six yards. It was somewhat intoxicated at this stage. The reason for this is the same as for the rabbit emerging from the ether narcosis. After two hours and ten minutes 0.2 cc. more of the sodium thiocyanate was injected subcutaneously. The rabbit held up its ears this time and hopped around, after first crawling a short distance. Every time that the sodium thiocyanate was administered after and including the injection at one hour and 42 minutes, the rabbit crawled around. From 58 minutes after the anesthetic was administered onward the animal was able to sit up of its own accord and did so. The animal passed considerable water after three hours and five minutes; it ate heartily after four hours five minutes and was quite happy so far as one could judge. Both of these rabbits were males.

It is interesting to note that the total dose of sodium thiocyanate in this case amounted to 450 milligrams per kilogram, or more than twice the dose that Kahn found was lethal to guinea pigs when using potassium thiocyanate.

These experiments show several interesting things; in the first place, they show the unusual degree of accuracy with which, with the developed Claude Bernard theory as the background, one is able to predict what will happen when a strong peptizing agent is introduced into a narcotized animal. Now, were the striking fact of the much accelerated recovery of the animal by the use of sodium thiocyanate entirely stricken from the experiment, there still remains a valuable observation. The rate of respiration of the rabbit that was subjected to the sodium thiocyanate treatment was more than twice as great as that of the control rabbit. What is the meaning of this? The lowered rate of respiration in the case of anesthesia is due to the effect of the anesthetic on the respiratory center in the brain; this effect is in all probability at least in part due to the coagulation of the colloids of the respiratory center. The displacement and peptizing action of the thiocyanate ion upon this center is, thus, quite marked. The result is that the respiratory center tends to regain normality very quickly as is shown by the data on the above experiments The value of this fact in preserving life is obvious.

The above rabbit which received the sodium thiocyanate injections was intoxicated for the same reason that the rabbit upon emergence from the ether narcosis hastened by thiocyanate ions was intoxicated. This intoxication affected the hind legs to a large extent in each of the two cases; and in the case of the controls they slipped through the excitation stage in each case too rapidly for it to be observed.

Thus, another and more powerful anesthetic has been found to yield with celerity to the displacing and peptizing effect of the thiocyanate ion upon the reversibly coagulated colloids of the sensory nerves of the central nervous system.

3. Morphine

This brings us to a study of the effect of sodium thiocyanate on that insidious alkaloid morphine. Morphine is, of course, a habit-forming drug; so, in this therapy there may be a clue to the solution of the problem of drug addition.

Taylor[1] says that morphine is probably slowly detoxicated, for it has been found unchanged in cadavers months after death as a result of an overdose. Spiegel[2] says that the site of the destruction of morphine in the body is mainly the brain. This also means that morphine is strongly adsorbed by the brain. Morphine slows down the rate of the heart beat; and one of the first effects of the drug in the body, in large doses is the paralysis of the respiratory center.[3] It is a matter of common knowledge that morphine affects various animals in different ways. For instance, the cat goes wild under its influence; it narcotizes some horses and with others it acts more as it does with the cat; rabbits require an unusually large dose to produce an effect;[4] whereas, a small dose will produce sleep in white people. These differences are undoubtedly due to varying degrees of adsorption on the nerve colloids of the various animals.

From these facts concerning morphine, what can be predicted concerning the action of sodium thiocyanate upon animals narcotized by means of it? Although the obstacles appear to be formidable, there are two experimental results that help to give us a clue as to what will happen in this case. Taylor[5] says that injections of starch have been found to be beneficial when there are signs of recovery from morphine poisoning; while Rother[6] found that starch can be used to prevent egg albumin from coagulating, even in boiling water. This means that the starch is adsorbed by, and acts as a protective colloid for, the egg albumin. The inference is obvious; in the case of morphine poisoning the starch probably displaces the morphine from the nerve colloids of the brain and then peptizes them. The other possibility that the starch adsorbs the morphine more strongly than do the brain colloids does not, however, become untenable, because of these facts. If starch peptizes the reversibly-coagulated nerve colloids of the brain in the presence of morphine it is decidedly not too much to expect that the thiocyanate ion will do the same. Since the respiratory center is affected by morphine (it has been shown that sodium thiocyanate tends to repeptize that center when the nerve colloids are reversibly coagulated by "amytal"), it is to be classed in the category of an entirely reasonable supposition that sodium thiocyanate will be of aid in relieving respiratory difficulties. Too much cannot be expected of sodium thiocyanate by way of rousing an animal out of morphine narcosis because the morphine is at least strongly adsorbed in the brain. The displacement of the drug from the nerve colloids of the brain by the adsorbed thiocyanate ions would not, therefore, make for any great increase in the rate of elimination of the drug.

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[1] "A Treatise on Poisons," 48 (1875).

[2] "Chemical Constitution and Physiological Action" 119 (1915).

[3] Gwathmey: "Anesthesia," 372, 643 (1914); see also Spiegel: loc. cit., p. 123.

[4] Crile: "A Bipolar Theory of Living Processes," 317, 320 (1926).

[5] "A Treatise on Poisons," 538 (1875).

[6] Kingzett: "Animal Chemistry," 380 (1878).

Morphine hydrochloride was used[1] in the experiments about to be described; it will be characterized as morphine. The first experiment that was made was done as a control. A water solution of morphine containing 0.12 grams of the drug was injected subcutaneously into a 2300 gram rabbit. The animal became dull in four minutes and was asleep in 12 minutes. The rabbit began to stir in 41 minutes; and it tried to rise after 59 minutes. It was not able to sit up after one hour and 14 minutes; at this time the animal lapsed back into a deep narcosis. The respiration was 12 per minute after three hours eight minutes. Shaking the rabbit produced no visible effect upon the narcosis. After three hours and 56 minutes the rabbit was turned over on its back; it stayed that way with its head thrown back and all of its legs stretched out at different angles for ten minutes. It was then laid over on its side again. Up to this time the animal had neither defecated nor urinated. The rabbit showed practically no resistance to severe mauling after four hours and 26 minutes; it kicked once upon being lifted by the ears. After five hours the respiration was only 18 per minute. The animal was left at two o'clock in the morning. At nine o'clock it appeared to be normal but somewhat washed out.

At the start of the above experiment, the companion rabbit to the one just described, weighing 2500 grams, was narcotized by morphine by a subcutaneous injection of 0.123 grams of morphine in water solution. The animal became dull in six minutes, and was asleep in ten minutes. When the narcosis became deep and definite, and the respiration was very low, (about 15 minutes after the morphine was administered) 3.8 cc. of a 10% solution of sodium thiocyanate was injected by the intravenous route. Eight minutes later the rabbit appeared to become conscious; it was able to sit up without trouble. The animal seemed to be in a dull stupor. One hour and three minutes after the injection of the morphine it seemed to lose strength somewhat; for that reason 3 cc. more of the sodium thiocyanate was injected intravenously. This procedure brought the rabbit back quickly. The respiration was 22 per minute after two hours and 35 minutes, as compared to 12 per minute for the control. Throughout the experiment the rate of respiration of the animal with sodium thiocyanate in it was twice as great as the respiration rate of the control. The rabbit was turned over on its back after three hours and 27 minutes; it kicked hard and turned over on its side. Repetition of the procedure brought the same result; finally the rabbit was put on its back and soothed (properly stroked, rabbits often go to sleep when in this position). Despite this the animal kicked very hard and determinedly until it was freed; then it turned over. Up to this time this rabbit had defecated quite a few times; whereas the control had not done so at all. This ratio was increased several fold at the time that the two animals were left. After four hours this rabbit strongly resisted mauling as compared to no resistance by the control. The animal kicked violently upon being lifted up by the ears four and one-half hours after the start of the experiment; at this time the respiration rate was 38 per minute as compared to 18 per minute for the control. The depth of narcosis that this animal was in was on the very border-line of consciousness from the time that the first injection of sodium thiocyanate was made; consciousness is elusive when one tries to define it for animals. Certainly the depth of narcosis of this rabbit was considerably less than that of the control. The animal appeared to be normal, but somewhat washed out when next seen at nine o'clock in the morning.

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[1] The authors wish to thank Prof. J. B. Sumner of the Biochemistry Department of the Cornell Medical College for supplying us with morphine hydrochloride.

The most evident conclusion that one can draw from these two experiments is that the thiocyanate ion tends to repeptize the reversibly coagulated nerve colloids of the respiratory center, for the respiration was much better in the case of the rabbit with sodium thiocyanate in it. Furthermore the state of narcosis produced by the morphine was visibly lessened by the presence of the sodium thiocyanate. So, the prediction that the thiocyanate ion would lessen the degree of narcosis and aid respiratory difficulties has been realized experimentally.

If one goes to the opposite end of the lyotropic series from the thiocyanate ion, the peptizing action of the anions there is nil. It is then that the cations become effective, and, as they are positively charged, they will tend to act as coagulants for a negatively charged protein sol. Therefore, one would expect that sodium tartrate (see the lyotropic series) would tend to act in the same direction as morphine; in other words it should prolong a morphine narcosis when injected into a rabbit.

The two rabbits that were used in the above experiments were prepared for the following experiments by feeding them heartily for a week and keeping them in the fresh air.

An intravenous injection of 5 cc. of a 10% solution of sodium tartrate was made on the 2300 gram rabbit. There was no visible ill effects from this treatment. Nine minutes later 0.10 gm. of morphine in distilled water was injected subcutaneously. Three minutes later the rabbit was strong and determined, but the rate of respiration was slowing down rapidly. After 15 minutes there was a distinct depression; the respiration rate was still falling rapidly, after 19 minutes it was very slow. This was accompanied by the exudation of saliva. Twenty-four minutes after the morphine was injected a good narcosis was observable. The rate of respiration was 30 per minute after 38 minutes; in one hour eight minutes the rabbit seemed to be in much better shape. The animal began to stir after one hour 39 minutes; it crawled around a bit after two hours. Ten minutes later it appeared to be approaching normal, but the rate of respiration was still down. The animal came a cropper, for it was extremely disinterested after four hours. After five hours the respiration rate was only ten per minute, as compared to 18 per minute after five hours when the animal had 0.128 gm. of morphine in it, and it was still in a narcosis. The rabbit appeared to be a little more nearly normal in five hours 33 minutes, but it was still in a poor condition after six hours 33 minutes.

From the above detailed description it would seem that this animal underwent a narcosis which was not quite so deep in its general aspect but which was as prolonged as when it was under the influence of 0.12 gm. of morphine, or a 16.7% greater amount of the drug. This can be ascribed to the action of the sodium ion as was predicted. So far as the respiratory center is concerned, it has been pointed out that there was a noteworthy improvement when using sodium thiocyanate.

In order to be more certain that the sodium tartrate had its own sensory-nerve coagulating effect the above rabbit was conditioned for a control experiment. After eight or nine days in the open air with plenty of food, the animal was injected subcutaneously with 0.1 gram of morphine in water solution. A slight depression was noticed within five minutes. After 18 minutes the rabbit was able to move its head unaided, but the morphine was beginning to have a profound effect. The breathing was very bad and irregular after 22 minutes. The animal refused to lie on its back after one hour and 40 minutes; its strength had returned, and it appeared to be quite conscious. The respiration rate was 18 per minute at this time. Four minutes later the animal arose of its own accord. In two hours 50 minutes it was strong, and completely conscious so far as could be judged; but it was unable to hop around. The animal was quite full of life after four hours and five minutes; it crawled around after four hours and 40 minutes. After five hours it was impossible to misjudge the fact that the rabbit was definitely and completely out of the narcosis; it was not very strong but it got around with ease and facility.

Comparing these last two experiments, it becomes evident that the animal came out of the morphine narcosis more quickly when there was no sodium tartrate in it. The narcosis was somewhat less deep and the period of recovery more sharp when the sodium tartrate was not present. So it seems that it has been clearly, although not strikingly, demonstrated that the sodium tartrate exerts its own narcotic effect which enhances the effect of the morphine. That the difference is not greater is very likely due to the sodium ion not being very strongly adsorbed as compared to the morphine.

At the time that the above rabbit was treated with sodium tartrate and morphine, the companion rabbit was treated with sodium thiocyanate and morphine. The 2500 gram rabbit was injected intravenously with 5 cc. of a 20% solution of sodium thiocyanate; this is roughly an equimolar amount with the sodium tartrate that was injected into the other rabbit at the same time. This caused a depression and rather queer pedal difficulties. The pedal idiosyncrasy was characterized by the fact that in attempting to move forward, about 50% of the time the net result was that the animal moved backward. This phenomenon is analogous to the effect of a subcutaneous injection of sodium thiocyanate into a normal rabbit when the rabbit hops into the air going forward at times and other times backwards. Fifteen minutes after the sodium thiocyanate was injected a subcutaneous injection was made of 0.1 gram of morphine in water solution. In two minutes the depression was greater; and in five minutes the animal was limp. During this time the usual large drop in respiration rate did not become manifest for the respiration remained rapid. So far as we could judge there was no loss of consciousness. The rate of respiration was 80 per minute 44 minutes after the morphine was administered; the animal still appeared to be conscious. At this time it was placed on its back, but it turned over of its own accord and proceeded to stretch. The animal was still conscious after one hour and 12 minutes. After one hour and 42 minutes a severe twitching of the neck, jaw, and head muscles was noticed. In a short time the twitching ran through the whole body. The animal acted as though it had chills. The convulsions became progressively more severe; the rabbit threw its head back and died after two hours and 17 minutes. There did not appear to be any tetanus and the animal seemingly never lost consciousness. As the rabbit was about to die peculiar ripples ran up and down its back on either side of the spinal column.

There are two obvious conclusions that can be drawn from this experiment; in the first place, the effect of morphine on the respiratory center can be very greatly diminished by the action of the thiocyanate ion upon the nerve colloids of that center. Witness the fact that the respiration rate did not decline before the above rabbit died, and in the case of the rabbit under the influence of morphine and sodium tartrate it was at one time only ten per minute as compared to 80 per minute for the above animal.

The experiment was a success but the rabbit died. Why? The symptoms were not those of morphine poisoning because so far as could be observed there was no loss of consciousness, and there was certainly no coma; furthermore the slow, deep breathing characteristic of the rabbit under a large dose of morphine was absent. There is ample support for the view that in the presence of the morphine the large amount of sodium introduced into the animal caused its death, the mechanism being a decrease in the amount of thiocyanate ions adsorbed, due to the coagulating effect of the morphine, with a consequent rise in the amount of sodium ions adsorbed, which ions work in the same direction as the morphine. Rabuteau[1] points out that potassium thiocyanate is a muscular poison, paralysis and death often being preceded by convulsions, but that the other salts of potassium are poisons and cause the same symptoms as potassium thiocyanate. In other words the poisonous action of this salt is due to the potassium: "On sût bientôt que le sulfocyanure de potassium agissait moins en qualité de sulfocyanure qu'en qualité de sel de potassium." He goes on to say that upon replacing the potassium atom by the sodium atom the effect in animals is very much less. In *high enough concentrations* sodium should act as a poison much like potassium. The presence of the morphine could conceivably cause the sodium to behave as though it were present in even higher concentrations than it was. On these grounds rests the case for the present.

The bearing of these experiments upon the problem of drug addiction is an inviting thesis. It is a natural corollary of this theory of anesthesia that

[1] "Éléments de Toxicologie," 498, 543-545, 547, 549 (1887).

the habitual user of drugs for the purpose of removing himself from the natural spheres of human society must, as a result, possess a brain in which the colloids of the sensory nerves are qualitatively constantly in a state of partial coagulation. Were these colloids peptized by a non-toxic dispersing agent so that they return either to their normal degree of dispersion or very close to it, normal brain function should ensue. The normal person is generally not a drug addict. Therefore, peptizing the nerve colloids of the brain should displace the drug, return the drug addict to a normal condition, relieve the desire for more, and result in a cure. It is not a necessary condition that sodium thiocyanate is the only compound that will produce these results, or that it will cure drug addicts at all. But, it is an enticing thought that perhaps it will; and almost certainly peptization therapy is the correct lead to follow, regardless of what compound is used. The compound that would be, according to this theory, useful in combating drug addiction should be water-soluble, strongly adsorbed by the brain and sensory nerve colloids, a good peptizing agent for protein sols, non-toxic, stable, not too quickly eliminated from the body, and preferable organic in nature.

In the light of our present knowledge of the action of morphine and sodium thiocyanate, it is entirely possible for the colloid chemist to make a good guess as to how one should go about treating drug addiction by means of sodium thiocyanate. Were addiction to drugs a psychological phenomenon, whatever that may mean, rather than a physiological colloidal change practically the same treatment would apply. The starting point for the treatment theoretically can be when the patient is in any one of the several conditions that one observes in addicts. Were the patient in imminent danger of death from morphine poisoning the first dose of sodium thiocyanate could be administered intravenously. McGuigan[1] states that intravenously 0.08 gm. of sodium thiocyanate per kilogram of body weight produces no toxic symptoms. Following this, the sodium thiocyanate could be given in small doses by mouth, progressively increasing the amount of the compound administered until a condition is obtained[2] in which there is, "disorientation, hallucinations of sight and hearing, mania, and ideas of persecution singly or in combination." This condition disappears shortly after the administration of the drug is discontinued. This, as will be shown in a later paper by Bancroft and Richter is the production of a neurotic condition by peptization of the brain colloids to a state greater than normal; that is, the colloidal micellae become smaller in size.

Dr. Norman S. Moore of Ithaca has brought to our attention the fact that the symptoms encountered upon withdrawal of morphine (apart from craving) from addicts resemble very closely those symptoms stated by Borg to be the result of prolonged administration of fairly large amounts of sodium thiocyanate. The normal state of the nerve colloids of the drug addict during the time that he is addicted is one of greater aggregation than that of the person who does not use morphine. Upon withdrawing morphine the natural peptizing agents of the body begin to work to break up the aggregates. There is thus a peptizing action which is in the direction of return to the state of an ordinary human being, and away from the state of partial aggregation that was normal during the time that morphine was used. Thereupon the mental symptoms appear. Sodium bromide, which is near the thiocyanate end of the lyotropic series, will relieve mental disturbances which are due to coagulation symptoms. Slight agglomeration or slight peptization of certain of the brain colloids cause much the same mental symptoms. Bancroft and Richter will discuss mental conditions more completely in a later paper.

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[1] "A Textbook of Pharmacology and Therapeutics," 102 (1928).

[2] Borg: Minnesota Med., 13, 293 (1930).

At the same time the quantity of morphine allowed the addict should be progressively decreased. If possible it would be well to discontinue the administration of morphine well before the neurotic symptoms due to the thiocyanate ion become manifest. Then as the neurotic symptoms disappear the sodium thiocyanate should again be commenced in small doses, for a short while, at the same time abstinence from the drug should be complete. The same sort of treatment should apply were the starting point the drug addict who is not in a state of coma.

As a result of such a treatment as this the brain colloids will theoretically be returned to their normal degree of peptization as a result of the action of the thiocyanate ion; that is after the neurotic condition has been attained and the thiocyanate treatment has been discontinued, this condition should obtain. The beauty of the direct employment of this therapy in humans is that the drug is fed slowly and at any signs of real distress the administration can be stopped before any permanent damage can be done. It will be increasingly apparent, as the story unfolds, that the danger involved in the proposed treatment is, barring outside complications, slight if not nonexistent. The only difficulty that can be foreseen is that due to the possible lowering of the blood pressure by the sodium thiocyanate. Perhaps ephedrine will circumvent this condition, should it arise, without interfering with the peptizing action of the thiocyanate ion.

4. Strychnine

"Strychnine[1] stimulates the spinal cord, increasing its reflex excitability, but it has little effect on the centers above the medulla. It stimulates the respiratory center, increasing the rate of respiration, but the effect is only temporary. Toxic doses raise the blood pressure by stimulating the vasoconstrictory center; it has little direct action on the heart. Poisonous doses cause tetanus, but the trismus is not marked. Between the attacks there is usually complete relaxation of the affected muscles. The convulsions are of spinal origin. Death may occur, during a convulsion, from fixation of the chest by spasm of the respiratory muscles or during the interval from respiratory paralysis."

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[1] Hatcher and Eggleston: "Useful Drugs," 139 (1926).

Now, if a given peptizing agent for proteins can make its way to the spinal cord, and provided it is adsorbed more strongly there than is strychnine, it will, according to this theory, displace the alkaloid, peptize the protein, and thereby tend to return that part of the nervous system to normal. Thus, sodium thiocyanate is obviously the first choice, on the basis of this theory, as the causative agent of a relief for strychnine poisoning. Accordingly a strychnine sulphate solution containing 0.03 grams per 100 cc. of distilled water was prepared. An 860-gram rabbit was injected intravenously with 0.86 cc. of this solution. Severe tetanic convulsions occurred almost immediately. In two and one-half minutes the rabbit was laid out by the convulsions. The animal exhibited severe dyspnea; it squealed loudly while in the convulsed state. The rabbit died in a great spasm eight minutes after the strychnine was administered. This was, of course, the control experiment. A litter-mate of the above rabbit, weighing 1000 grams, was injected intravenously with 1.1 cc. of a 10% solution of sodium thiocyanate. After seven minutes had elapsed one cc. of the above strychnine solution was injected intravenously. Tetanic stimulation came on immediately; this time it was not nearly so severe, and was spasmodic rather than continuous as in the control. No dyspnea was manifest; the breathing was regular. The tetanic stimulation ceased in three or four minutes; and in nine minutes strong clonic movements were observed. After 17 minutes from the time that the strychnine was administered, the clonic movements suddenly landed the rabbit erect on its feet. Three minutes later the animal appeared to be almost normal. At this time it partook of water when it was offered, and nibbled lightly at grass. This animal did not squeal at all. The rabbit was well and happy 24 hours later.

Thus, another portion of the central nervous system is brought into accord with the general theory. Since strychnine can also be made to act as an anesthetic,[1] it requires no stretching of the imagination to see that strychnine acts upon the sensory nerve colloids in such a manner as to cause coagulation. The theory is vindicated by the action of one more drug.

Chloroform and some other general anesthetics are well known as antagonists for strychnine poisoning. This may be cited as evidence against the validity of this theory of the colloidal behavior of the central nervous system, for chloroform is also a coagulant. The answer is easy. Chloroform must be more strongly adsorbed by the proteins of the sensory nerves than is strychnine. As a result the strychnine is displaced by the chloroform which, although it is more strongly adsorbed, is not so good a coagulant, and eliminated by the body. The chloroform is then, in its turn, also eliminated. The more strongly adsorbed substance is not necessarily the better coagulating agent, for the rate and amount of coagulation are functions of the degree that electrokinetic potential of the charged micellae is lowered by the coagulating substance.

One finds[2] that potassium thiocyanate precipitates strychnine from solutions of its salts when the concentrations are right, by forming an insoluble strychnine thiocyanate. However, it is fairly certain that this is not the mechanism of the experimental results reported here; for with a solution such as was used, one fails to observe a precipitation upon adding an equal volume of a 10% sodium thiocyanate solution.

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[1] Bancroft and Richter: Proc. Nat. Acad. Sci., **16**, 574 (1930).

[2] Wormley: "Micro-chemistry of Poisons," 575 (1885).

5. Alcohol

This brings us to a study of the effect of sodium thiocyanate upon the action of ethyl alcohol. As one ordinarily observes the action of alcohol, the period of stimulation is distinctly greater than with the ordinary anesthetics. With fish it can be demonstrated that under comparable conditions the period of stimulation in an alcohol solution is longer than in an ether solution. May[1] states that, "the chief action of ethyl alcohol is on the nervous system, the narcotic effect being preceded by a loss of control of the higher centers, an effect which has led to the mistaken belief that alcohol in small quantities acts as a stimulant." While holding no brief for the medicinal use of alcohol as a stimulant, it does seem somewhat useless to argue that stimulation is not one of the physiological effects; certainly there may be vocal stimulation. May becomes more interesting on page 49. "The action of certain substances, such as alcohol cannot be explained by the foregoing theories [Meyer-Overton, and others]. Alcohol is miscible with water in all proportions, and is only slightly soluble in fats, but this need occasion no surprise when it is borne in mind that alcohol does not really belong to the same class of substances as sulphonal and inert bodies of that type, as it exerts some action on proteins and is oxidized in the body. The action of alcohol is, therefore, probably specific, and of a different kind from that of sulphonal, etc."

From the general considerations of the case there does not appear to be any outstanding reason why sodium thiocyanate should not exert some antagonistic effect upon the action of alcohol.

The first experiment[2] was performed on a young 8.0 kg. female dog. Approximately 14 cc. of 95% alcohol was diluted with about three times its volume of water and administered per os. The alcohol took effect in nine to ten minutes. Ten minutes after the alcohol was administered 15 cc. of a 10% solution of sodium thiocyanate was injected intravenously at the approximate rate of one cc. per minute. During the injection, which was done under a local anesthetic, the dog's head hung over the side of the operating table. By the time that the injection was finished the animal showed more interest in life. Twenty minutes after the injection the dog was sober again. No depression was noted at any time after the injection.

As a result of experiments with rabbits, it would appear that both by the intravenous injection and inhalation methods it takes a great deal of ethyl alcohol to produce anesthesia. A 2100 gram rabbit was kept for four hours in a closed space in an atmosphere containing alcohol vapor. This did not seem to affect the animal; so it was removed and placed in a much smaller closed space containing what to a human being would be almost a suffocating concentration of alcohol vapor. After one and one-half hours in the strong atmosphere the animal was removed. It was quite intoxicated; that is, it could hardly hop, and when placed on its side was content to remain so. These observations consumed about five minutes. The rabbit was then put back into the alcohol chamber into which more alcohol vapor was introduced. Fifteen minutes thereafter the rabbit was removed and two cc. of a 10% solution of sodium thiocyanate was administered intravenously. This was followed immediately by a subcutaneous injection of six cc. of the same solution. The rabbit remained intoxicated, but hopped around a great deal. It would not repose upon its side when so placed.

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[1] "Synthetic Drugs," 23 (1921).

[2] Our thanks are gratefully extended to Dr. H. C. Stephenson, Professor of Materia Medica in the New York State Veterinary College at Cornell University for performing this and other experiments at our request.

Two persons volunteered to become intoxicated and then take sodium thiocyanate.[1] One of the volunteers ingested the equivalent of approximately 275 cc. of alcohol; while the other consumed the equivalent of approximately 175 cc. of alcohol. In the space of three quarters of an hour the two persons took respectively four and three grams of sodium thiocyanate in water solution, a gram at a time.

The general results of this experiment were several. In the first place, the dilatation of the pupils of the eyes had decreased noticeably fifteen minutes after the sodium thiocyanate was taken; shortly after this there was a marked decrease in the apathetic euphoria in both cases. Over a period of 70 minutes the pulse rate went steadily down from 92 to 72 and from 76 to 70 respectively. The two persons were kept quiet throughout, and neither lost consciousness. The rate of respiration tended to rise slightly in each case.

Thus, with ethyl alcohol there were no very striking results observed. But, that there was some antagonism between the sodium thiocyanate and the alcohol seems certain, although quantitatively it was not very much. It does not appear, on the surface, that it should be very difficult to demonstrate in a somewhat more dramatic manner the antagonism between these two compounds. We are working on this problem at present.

6. "Nembutal"

"Nembutal," sodium ethyl (1-methyl butyl) barbiturate, is an isomer of "Sodium Amytal." One would naturally predict that since "amytal" yields to sodium thiocyanate therapy, "nembutal" might also fall in line. The results of a brief study indicate that this is not quite the case. Dr. Stephenson tried an experiment upon a dog such as those reported under "Amytal" which was not successful. Unsuccessful experiments upon rabbits and goldfish have also been made.

The apparent reason for the failure of sodium thiocyanate in this case is that the "nembutal" is more strongly adsorbed than is "amytal." As a result it would be more difficult for the thiocyanate ion to displace the adsorbed anesthetic. More reasonableness is lent to this view when one considers that 40 to 50 mg. of "sodium amytal" per kilogram of body weight injected intravenously produces in dogs a surgical anesthesia which lasts for from one to three hours,[1] whereas, Dr. H. C. Stephenson[2] says that 25 mg. of "nembutal" per kilogram of body weight, injected intraperitoreally, will produce in dogs a surgical anesthesia which lasts for from one to three hours. Since "nembutal" requires only one-half the amount that "amytal" does to produce surgical anesthesia in dogs, one seems to have as the best explanation on the basis of this theory that alternative which we have chosen.

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[1] The authors extend their sincere thanks to Barton F. Hauenstein, M.D., Tompkins County Pathologist, who so kindly conducted these experiments. They also duly thank the volunteers.

7. Anaphylaxis

The case of anaphylaxis involves a shift from the central nervous system to the sympathetic nervous system. One is impressed by the multitude of different reactions found under the general headings of anaphylaxis, anaphylactoid reaction, and allergy with their various symptomatological manifestations. So wide is the field that Wells[3] has been lead to define true anaphylaxis rather rigidly. On the other hand, we find the statement[4] that, "the symptomatology of the reactions following the introduction of any serum, vaccine, protein substance and colloid is always the same: it is the symptomatology of colloid or humoral shock." Lumière[5] says: "Our colloidal theory of life and disease enables us readily to understand this community of symptoms. All these pathogenic agents, however they may differ have one property in common: they determine the flocculation of certain humoral colloids whose coagulation produces the pathological symptoms." Despite the fact that anaphylaxis is not due to a humoral reaction,[6] the flocculation and peptization structure of the statements of Kopaczewski and Lumière appear to hold for the case in hand.

While in anaphylaxis and the various forms of allergy one notes certain symptoms in common, they are not necessarily quantitatively alike, nor are all of the symptoms of one affection present in the cases of all of the other affections. This is hardly to be wondered at when one considers that the efferent sympathetic nervous system has communication with and is distributed in the eyes, mucous membranes of the nose, the palate, the parotids, the heart, the larynx, the trachea, the bronchii, the lungs, the esophagus, the stomach, abdominal blood vessels, the liver and ducts, the pancreas, the adrenals, both intestines, the kidneys, the bladder, etc.[7] Thus, purely on the grounds of chance a silver sol, for instance, would be more strongly adsorbed on some of these substrates than on others, and also, it probably would be adsorbed quantitatively differently from an albumin sol. Even though the sympathetic nerve colloids in all parts of the body were chemically the same, their physico-chemical conditions could be different, due to being bathed in different amounts of different electrolytes.

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[1] Clowes, et al: Proc. Soc. Exp. Biol. Med., **26**, 399 (1929).

[2] Private communication concerning a long series of experimental results.

[3] "The Chemical Aspects of Immunity," 228 (1929).

[4] Kopaczewski: Alexander's "Colloid Chemistry," **2**, 968 (1928).

[5] Alexander's "Colloid Chemistry," **2**, 688 (1928).

[6] "The Chemical Aspects of Immunity," 234 (1928).

[7] Gray: "Anatomy of the Human Body," 967 (1930).

If, as seems probable, anaphylaxis is intimately associated with the flocculation or peptization of the colloidal proteins of the sympathetic nervous system, it is not too much to expect that sodium thiocyanate will either relieve or aggravate the condition markedly. Especially is this so when one considers that the sympathetic nerves are exposed.

An 800 gram rabbit was sensitized by injecting one cc. of a sterile 22% egg white sol (22 cc. of fresh egg white mixed with 78 cc. of distilled water) subcutaneously.[1] Twenty-one days later 0.8 cc. of a 10% solution of sodium thiocyanate was injected intravenously. Twenty minutes later two cc. of a sterile 22% egg white sol was administered by the same route. None of the symptoms of anaphylaxis were observed in this rabbit.

The control rabbit was a litter-mate of the above; they were both sensitized at the same time with the same amount of the same 22% egg white sol. The antigen was introduced into this animal a few hours before the above rabbit was injected. The technique and amount were identical. A typical but mild shock was observed, from which the rabbit apparently recovered in about three quarters of an hour.

A third litter-mate of the above rabbits that was sensitized at the same time in the same way was injected intravenously with 2 cc. of a 22% egg white sol mixed with 0.8 cc. of a 10% sodium thiocyanate solution. There was severe dyspnea and probably tetanic convulsions (they could not be seen because the body was inclosed during the injection); the animal died within a minute after injection. The following symptoms were observed: marked depression, body limp, increasingly weaker heart beat, irregular respiration with dyspnea, protruding eyes which became fixed. No defecation or urination was noticed during the minute that the rabbit lived. Upon picking the dead rabbit up it became obvious that contraction of the bladder and intestines had taken place. A post-mortem examination revealed that both intestines were constricted. Also the sigmoid colon, rectum, gall bladder, bladder, and the abdominal arteries were constricted. The left ventricle was in systole; there were no apparent signs of disease.

These experiments, in addition to two others in which rabbits, apparently about to die from anaphylaxis, were rapidly revived by the use of sodium thiocyanate, leave little doubt that here again it is a question of coagulation and peptization. ·Exactly what phenomena take place, and their order of occurrence are questions that are reserved for a later paper on the mechanism of anaphylactic shock.

Karsner[2] says: "Drugs which depress smooth muscle excitability, those which depress nerve activity generally [note the parallelism to Claude Bernard's theory of narcosis], in the group of narcotics and anesthetics, those which tend to maintain blood pressure, are pharmacologically adapted to the inhibition or even prevention of shock. Thus atropin, adrenalin, chloral hydrate, ether, alcohol, atoxyl, and numerous other drugs have been employed."

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[1] The authors wish to thank Mr. William B. Stocking for his assistance with this work.

[2] Karsner, in Jordan and Falk: "The Newer Knowledge of Bacteriology and Immunology," 978 (1928).

These drugs are of course diametrically opposite in their action to sodium thiocyanate, provided the adsorption of the thiocyanate is upon negatively charged sympathetic nerve colloids, and provided the lyotropic series for the active protein is the same as it is for egg albumin. Still it is conceivable that anaphylaxis can be prevented either by peptization or coagulation.

8. Histamine

Histamine causes a reaction very much like that of anaphylaxis.[1] "Not only does histamine cause bronchial spasm in guinea pigs, obstruction to pulmonary circulation in rabbits, and fall of blood pressure in dogs, but applied to the skin or mucous membranes, it causes marked local urticaria resembling closely that of skin reactions in sensitized persons, and it does all these things in extremely minute dosage, comparable with the dosage of proteins used in anaphylactic reactions."

Delbet[2] says that histamine acts upon the same substrates as does a protein in causing anaphylaxis. However, in true anaphylaxis there is a distinct decrease in the coagulability of the blood; this change[3] is not apparent in the case of histamine shock.[4]

So, histamine, acting on the colloids of the sympathetic nervous system, probably has a more direct and less complicated colloidal effect, not being in colloidal suspension itself, than is met with in the antigen-antibody actions. Assuming, therefore, that histamine is either directly or indirectly responsible for the coagulation, and the possible complicating circumstances, of sympathetic nerve colloids, one can predict the effect of sodium thiocyanate upon its action. Depending upon the type of colloid met with in the case of the sympathetic nerve proteins, sodium thiocyanate should either increase or decrease the action of histamine. That is, were the colloids with which we are dealing positively charged the action of the histamine should be intensified; whereas were they negative, and were the lyotropic series not reversed, the sodium thiocyanate should decrease or inhibit the action of histamine.

One cc. of a solution of histamine dihydrochloride containing three milligrams per cc. was injected intravenously into a rabbit weighing 930 grams. The effect was very rapid, for the rabbit was dead in about four minutes. The obvious symptom was severe convulsions.

A 790 gram rabbit was given 1.1 cc. of a 10% solution of sodium thiocyanate intravenously. Fourteen minutes later, 0.85 cc. of the same histamine solution was injected by the same route. This time, instead of the rapid appearance of violent convulsions, the striking thing was that no outward symptoms of shock appeared; no symptoms of any kind were observed.

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[1] Wells: "The Chemical Aspects of Immunity," 240 (1929).

[2] Rev. Chir., 57, 309 (1919); Wells: "The Chemical Aspects of Immunity," 241 (1929).

[3] Achard and Aynaud: Compt. rend. Soç. Biol., 67, 83 (1909); Lee and Vincent: J. Med. Res., 32, 445 (1915); Pepper and Krumbhaar: J. Infect. Dis., 14, 476 (1914).

[4] Smith: J. Immunol., 5, 239 (1920).

This is even more striking when one considers that sodium thiocyanate has been shown to act upon nerve colloids in the opposite way to anesthetics. The drama of the situation is increased when one takes into account the fact that a litter-mate of the above rabbits weighing about 790 grams died quickly from the effect of 0.2 cc. of the above histamine solution.

Thus it is that histamine falls into line with the general theory that protein coagulation is the cause of various changes in living tissue, whereas, protein peptization is the cause of the reversal of these changes. Since the exposed sympathetic nerves are said not to be coated by lipoids, these experiments deal a sharp blow to the idea that lipoid disturbance plays a significant part in anesthesia.

9. Some Experiments in Vitro

If one works with things known to have little or no secondary or by-effects there seems to be no real theoretical reason why many, if not all, of the drug actions falling into classes of those reported in this paper should not be studied *in vitro*. The ground has been broken for this type of study. It has been shown[1] that a slightly acidified albumin sol, to which sodium sulphate has been added, flocculated upon the addition of small amounts of an alcohol or chloral hydrate. Edestin, under similar conditions, was not sensitized as much as albumin. Likewise, calcium chloride sensitized an albumin sol to alcohol. "This shows that this sensitization is specific both for different narcotics and substrates and is in line with the fact that all narcotics do not affect the same tissues equally."

Bancroft and Richter continue: "In the experiments where the protein sols were sensitized by ether to electrolytes it was found that at the beginning of the decrease in dispersion the phenomenon was reversible. That is, if the ether is removed by blowing a stream of air through the solution, the turbidity is decreased. At a later stage when the albumin has been precipitated, the precipitate can be removed by filtration and partially repeptized in a solution of the same composition as the original except that the ether is absent. This peptization becomes increasingly difficult if the ether is allowed to act for longer lengths of time."

An albumin sol sensitized by electrolytes and partially coagulated by ether cleared up again when sodium thiocyanate was added to the system.

Binz[2] has shown that sections of the brain cortex of rabbits coagulate when immersed in a 1% solution of morphine hydrochloride. If the coagulation was not allowed to proceed too far, peptization was accomplished by merely washing out the morphine.

By layering one liquid against the other, as in the precipitin test, it was found that histamine dihydrochloride caused a sterile horse serum sol to precipitate at the liquid-liquid interface. This was not due to the absence of the proper amounts of electrolytes with the resultant possible precipitation of globulin for when pure water was layered against the sol there was no precipitation. Likewise a negatively charged silver sol gave a very heavy precipitate with sterile horse serum.

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[1] Bancroft and Richter: J. Phys. Chem., 35, 227 (1931).

[2] Gwathmey: "Anesthesia," 34 (1914).

Such studies as these give us a clue to the anaphylactoid reaction due to "Electrargol" and "Collargol." By reducing a solution of silver nitrate with ferrous sulphate in the presence of citric acid a negatively charged silver sol is formed; when one cc. of such a sol (after dialysis) was injected intravenously into a rabbit weighing about 900 grams, it immediately caused convulsions, clonic movements, and dyspnea. Thus, an anaphylactoid reaction is observed. The particular role that this experiment plays in the general line-up is that it shows that the reactions of "Electrargol" and "Collargol" are not necessarily due to protein products adsorbed thereon. In cases such as this, the reaction may be to a large extent of a humoral nature; for when one adds such a silver sol as the above to sterile horse serum a great deal of visible coagulation takes place.

Urethane, which is an anesthetic, caused a slightly sensitized egg albumin sol to precipitate; on the other hand, it lowered the temperature of jelly formation of a 10% gelatin jelly. This raises the strong suspicion that anesthesia of the sensory nerves does not depend upon colloids of the gelatin type where the water equilibrium plays a dominant part in determining the degree of dispersion of the sol.

It is not claimed, as a result of these experiments, that a colloidal system has been found that will respond to coagulation and peptization in a manner analogous to that of the sensory nerve colloids. For instance in the cases of the artificially sensitized albumin sols, the systems were slightly acid; in such cases sodium thiocyanate itself is a coagulating agent for the sol. The important thing is that by choosing a protein sol that is coagulated to a greater or lesser extent by anesthetics in general, and which is peptized strongly by the thiocyanate ion, one should be able to study quite thoroughly the quantitative side of anesthesia, the theoretical side of which is now on a firm basis.

General Considerations

Lest misunderstandings arise, it is well to consider what the purpose of this paper is. The prime motive is to establish even more firmly by experiments *in vivo* that the colloidal coagulation theory of narcosis is the correct explanation of the direct facts met with in anesthesia and certain other physiological conditions. No effort is made to show that in any given case sodium thiocyanate will alleviate the conditions dealt with at any *given* greater rate than would normally obtain. For instance, it makes little or no difference theoretically whether sodium thiocyanate causes a rabbit to come out of "amytal" anesthesia 100% sooner than normal or 1% sooner than it ordinarily would. The main thing is that it does cause the animal to return to consciousness in a shorter period of time than when no peptizing agent is present. In other words the quantitative side is not important, but the presence of a colloidal antagonism is. A drug is not being offered for immediate clinical use, although there are indications that it may be of value in certain conditions other than hypertension. This thesis will be more fully considered in the next paper.

A plea is made for peptization therapy as being the correct theoretical line to follow in the case of some specified physiological conditions. If sodium thiocyanate is not an efficient enough peptizing agent for employment in clinical practice there do not seem to be any great barriers to the preparation of a non-toxic organic compound which is better in that respect, although in any case the appearance of transient toxic psychoses should not be wondered at. In the ordinary course of events this task should not necessarily be up to the physical chemist.

Since this paper is not concerned with an exhaustive study of the pharmacological properties of sodium thiocyanate, it has been deemed sufficient to perform one control experiment along with each experiment on antagonism. The question of biological variation does not, therefore, logically enter into the situation. The strength of the case that has been built up lies to a appreciable extent in the completeness with which a variety of drugs behave toward sodium thiocyanate as one would predict in advance that they should. At the same time, it should be pointed out that if a given drug is not antagonized by sodium thiocyanate, that fact is not a proof that the drug does not act by coagulation. In other words, lack of antagonism to a given drug by sodium thiocyanate does not characterize the action of that drug. All that it shows is that the drug is so strongly adsorbed by the nerve colloids that the thiocyanate ion is not able to displace it effectively, or else the drug does not have a direct action; yet again the drug might be acting upon substrates that are inaccessible to the sodium thiocyanate. A drug may bring about irreversible coagulation; in such a case antagonism by sodium thiocyanate is a paradox. However, each drug that is known to act upon the nervous system which is antagonized by sodium thiocyanate is just one more building block on the superstructure of this theory of anesthesia.

It is not amiss to point out again that in all probability we are not dealing with coagulation that can be observed with the unaided eye; in such cases coalescence is likely to intervene and cause a coagulation the reversal of which would demand drastic means. In the cases such as we are dealing with the nerve protein colloids probably only agglomerate forming slightly larger particles.

The trail has been blazed; let those follow who will.

The general conclusions supported by this paper are as follows:

1. *In vivo* application of Claude Bernard's theory of narcosis as developed by Bancroft and Richter has been made successfully.

2. Sodium thiocyanate has been found to be a valuable antagonist for the study of ether, "amytal," and morphine narcoses, strychnine and histamine poisoning, and anaphylaxis.

3. Sodium thiocyanate relieves to greater or lesser extents the effects of these drugs.

4. The action of the sodium thiocyanate is due to the thiocyanate ion.

5. The thiocyanate ion peptizes the colloids that are coagulated by the above-mentioned drugs.

6. The cycle, stimulation, anesthesia, stimulation, normal condition has been observed experimentally.

7. The period of stimulation upon forced recovery due to the thiocyanate ion is somewhat exaggerated; this phenomenon is explained on the coagulation and peptization theory. It is a natural consequence of the existing state of affairs in the recovering animal.

8. The way has been opened for the relief of the long post-operative anesthesia due to "amytal."

9. "Nembutal" is probably more strongly adsorbed by the protein colloids of the sensory nerves than is "amytal."

10. Sodium thiocyanate apparently peptizes the colloids of the respiratory center.

11. A theory, and a treatment based thereon, for the relief of drug addiction has been proposed. The theory is based on peptization of coagulated protein colloids of the brain.

12. Sodium thiocyanate may give relief to drug addicts. If this is not the case, the properties of a compound that will so do (based on the general theory of anesthesia) have been elucidated.

13. There is apparently a lyotropic series of ions, as there should be, connected with the peptization of the colloids that are coagulated by morphine. This is supported by the fact that sodium tartrate augments the action of morphine whereas sodium thiocyanate tends to antagonize it.

14. The use of too much sodium thiocyanate in the presence of a strong narotic may cause sodium poisoning.

15. Sodium and potassium are not interchangeable, when administering drugs.

16. Alcohol appears to be antagonized only slightly by sodium thiocyanate.

17. Under ordinary conditions there is no noticeable antagonism to "nembutal" by sodium thiocyanate.

18. The intensity of strychnine poisoning is lessened markedly by the thiocyanate ion.

19. Complete protection against a large dose of histamine has been observed.

20. Sodium thiocyanate has been found to protect rabbits against anaphylactic shock. A peptizing agent as well as coagulating agents (anesthetics) therefore counteracts anaphylaxis.

21. The thiocyanate ion has been shown to act upon the protein colloids of the central nervous system including the brain and spinal cord, and the sympathetic nervous system.

22. The value of experiments with proteins *in vitro* with compounds affecting the nervous systems and with peptizing agents has been pointed out. Examples of the actions have been given.

23. The possible therapeutic value of sodium thiocyanate in treating coagulated conditions of the nervous systems has been pointed out, although no extended pharmacological investigation of the compound has been made.

24. No evidence has been found or adduced that the lipoids play a dominant role in the phenomena studied.

25. Claude Bernard's theory of anesthesia as developed by Bancroft and Richter has been found to be inescapable.

Cornell University.

THE INFLUENCE OF THE PROXIMITY OF A SOLID WALL ON THE CONSISTENCY OF VISCOUS AND PLASTIC MATERIALS. III

It has been recognized for some time that, if a paste of clay or soil in water is forced through a narrow tube, there are certain limits of pressure between which the flow is telescopic. Within this range the rate of increase of extrusion with increase of pressure is constant within the present limits of experimental accuracy. Except in the case of very thin pastes the straight line obtained by plotting the volume V extruded in unit time against the pressure P does not on extrapolation pass through the origin, but makes a positive intercept on the pressure axis. Nevertheless, according to the treatment of Bingham[1] as amended by Buckingham[2] and independently by Reiner[3] the slope of this line should give the mobility of the material, a constant of which the reciprocal is closely analogous to the viscosity of a true fluid and has therefore been called the pseudo-viscosity.

In an investigation described in the first paper of this series[4] it was found that with many pastes the value obtained for the mobility from Bingham's equation depended upon the diameter of the tube used. It was shown that this result could only be accounted for by supposing a layer of material near the wall of the tube to have a mobility different from that of the bulk of the paste passing through the centre of the tube. It appeared sufficient for the purpose of obtaining this true mobility to assume that the thickness of the modified layer is small in comparison with the radius of the tube. Since the discrepancies are often considerable, it is desirable to obtain assurance on this point, or failing this, to form an estimate of the error that may be introduced in cases where the modified layer forms an appreciable fraction of the radius of the tube.

An attack was made on this in a second paper.[5] The method used, though direct, was rather cumbersome and was not quite complete.** The following treatment is more concise and enables the implications to be more clearly set out.

Imagine that a material of mobility μ_ω is flowing through a tube of radius R, and that the line ACB in Fig. 1 represents, by the distance above AB, the velocity distribution within the tube. This curve is of course a section of a surface which can be traced within the tube, and the volume enclosed between this surface and the cross-section at AB is a measure of the volume extruded in unit time. If now it be supposed that, instead of a constant mobility across the tube, the value μ_ω only holds between the wall and an imaginary cylindrical boundary distant δ from it, and that within this boundary the mobility is μ_0, the surface within the boundary will have a section represented by the line ADB. The total extrusion will, in this case, be less than that in the first case by an amount given by the volume enclosed between the two curved surfaces. This volume may be taken to represent an extrusion through a tube of radius $(R - \delta)$.

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**In giving an expression for the velocity of a point within the bulk of the material, the velocity given was that relative to the boundary distant δ from the wall (the symbol r' was used in the earlier paper). There should also have been a term in addition to allow for the velocity of the boundary relative to the wall of the tube.

Within the pressure range over which the flow curves are straight, its slope dV/dP has, for the case where the mobility is μ_ω over the whole cross-section, a value

$$dV/dP = \frac{\pi R^4}{8L}\mu_\omega$$

L being the length of the tube which is long in comparison with its radius R.

To obtain the slope of the flow curve in the second case an amount must be subtracted equal to the rate of change with P of the volume enclosed between the two curved surfaces of Fig. 1. This is

$$\frac{\pi(R - \delta)^4}{8L}(\mu_\omega - \mu_0)$$

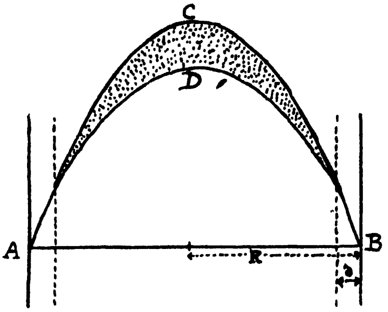

FIG. 1

Thus in the second case

$$dV/dP = \frac{\pi R^4}{8L}\mu_\omega - \frac{\pi(R - \delta)^4}{8L}(\mu_\omega - \mu_0)$$

The slope σ of the graph of mean velocity of extrusion $(V/\pi R^2)$ against stress on the wall of the tube $(PR/2L)$, used in the earlier papers, is readily obtained by multiplying both sides by $2L/\pi R^3$

$$\text{thus } \sigma = \frac{d(V/\pi R^2)}{d(PR/2L)} = \frac{2L}{\pi R^3}\cdot\frac{dV}{dP} = \tfrac{1}{4}R\mu_\omega - \tfrac{1}{4}\frac{(R - \delta)^4}{R^3}(\mu_\omega - \mu_0)$$

If now we suppose that the change from μ_ω to μ_0 does not take place abruptly at a fixed distance δ, but that the mobility at a point in the tube is a function of its distance δ from the wall (but not of R), the expression for σ becomes

$$\sigma = \tfrac{1}{4}R\mu_\omega - \tfrac{1}{4}\int_{\mu_\omega}^{\mu_0}\frac{(R - \delta)^4}{R^3}d\mu$$

provided that μ reaches the constant value μ_0 before δ reaches R. On expansion this becomes

$$\sigma = \tfrac{1}{4}R\mu_\omega - \tfrac{1}{4}\int_{\mu_\omega}^{\mu_0} R\,d\mu + \int_{\mu_\omega}^{\mu_0}\delta\,d\mu - \tfrac{3}{2}\int_{\mu_\omega}^{\mu_0}\frac{\delta^2}{R}d\mu + \text{etc.}$$

$$= \tfrac{1}{4}\,R\mu_0 + \int_{\mu_\omega}^{\mu_0} \delta d\mu - \frac{3}{2R}\int_{\mu_\omega}^{\mu_0} \delta^2 d\mu + \text{etc.}$$

According to this expression the graph σ against R should be of the type shown by the full line in Fig. 2. At high values of R, the curve approaches an assymptote which has a slope $\frac{1}{4}\mu_0$ and which is represented by the broken line. The departure of the actual curve from this assymptote depends on the relative magnitudes of R and $\bar{\delta} = \int \delta^2 d\mu / \int \delta d\mu$. Although no sharp boundary has been assumed to exist between the bulk of the material and the modified layer, nevertheless $\bar{\delta}$ is a kind of effective thickness of the modified layer near the wall. The assymptote was drawn in by inspection to give a convenient intercept on the σ axis. The position of the curve was then calculated assuming a value for $\bar{\delta}$ equal to 8×10^{-3} cm. (being 20 per cent of the radius of the smallest tube used in the experimental work). The experimental points are for the Broadbalk field subsoil for which the full data were given in the first paper. It is evident that although a straight line could fairly be drawn through the points, as was done in the earlier paper, the experimental uncertainty is such that the possibility of a slight curvature is not ruled out. Actually a number of curves could be drawn each of which would pass sufficiently near the points so that the position of the assymptote is to some extent arbitrary.

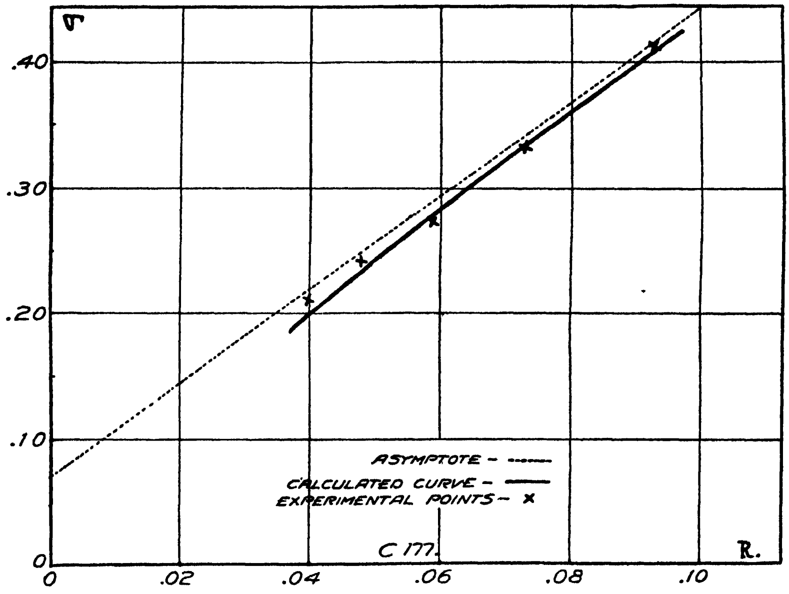

FIG. 2

Conclusions

An examination of all our data shows that no reliable estimate can be made of the curvature of the $\sigma - R$ graphs and thus no evaluation of $\bar{\delta}$ is yet possible. At the same time it is apparent that a value of $\bar{\delta}$ amounting to 8×10^{-3} cm. could escape detection owing to present experimental uncertainties.

Were it possible to draw the true assymptote, its intercept on the σ axis would, according to the forgoing analysis, give the value of $\int_{\mu_\omega}^{\mu_0} \delta d\mu$. The intercept made by the best straight line through the points, which we have called σ_0 is evidently somewhat less than this.

With regard to the value of μ_0, the mobility of the material in bulk, we may conclude that although a determination based on the slope of the best straight line drawn through experimental points on the $\sigma - R$ diagram is more accurate than any value calculated by the Bingham formula for a single tube, the value may still be a little too low owing to a finite thickness of the modified layer.

Summary

Evidence was obtained in an earlier paper that, when a clay or soil paste is forced through a narrow tube, a layer of material next to the wall has a consistency different from that of the bulk of the material. It was first assumed, for simplicity of treatment, that the modified layer is very thin compared with the radius of the tube; but later an attempt was made to remove this restriction.

A simpler and more complete treatment is now given, and it is concluded that a solid wall may modify the consistency of the material at an appreciable distance from it, but that the accuracy of the available data is insufficient to enable any reliable estimate to be made of the thickness of the modified layer. It is shown that, even when its effective thickness is as much as 20 per cent of the radius of the tube, the construction proposed in the first paper for determining the mobility of the material in bulk gives a close approximation to the true value. A full application of the extended treatment must await the development of more accurate experimental methods.

Bibliography

[1] E. C. Bingham: "Fluidity and Plasticity" (1922).
[2] E. Buckingham: J. Am. Soc. Test. Mat., **1921**, 1154.
[3] M. Reiner: Kolloid-Z., **38**, 80 etc. (1926).
[4] R. K. Schofield and G. W. Scott Blair: J. Phys. Chem., **34**, 248 (1930).
[5] G. W. Scott Blair: J. Phys. Chem., **34**, 1505 (1930).

THE APPLICATION OF X-RAYS TO CHEMICAL PROBLEMS*

BY MAURICE L. HUGGINS

The great importance of x-rays in medicine and surgery is well known to nearly everyone, and most of us are at least vaguely familiar with the use of x-rays in arriving at the arrangements of atoms and molecules in crystals. The many ways in which x-rays can be of service to chemists, however, are little realized. What seem to the writer the most important of these will be sketched in this paper.

Let us start by considering the usefulness of analyses of crystal structures. In the first place they furnish evidence regarding the structures of the component atoms, for it is these structures which determine the type of arrangement in the crystal. For instance, iodine crystals contain diatomic groups, each atom adjacent to but one other; selenium and tellurium crystals contain strings of atoms, each atom having two neighbors; arsenic, antimony and bismuth crystallize in puckered layers, in which each atom is equidistant from three others; while in the diamond structure each atom is surrounded by four others. These facts furnish strong evidence for the existence of 7, 6, 5, and 4 valence electrons, respectively, per atom in these various types and for the tendency of electronegative atoms to share pairs of valence electrons until each has a complete octet around its atomic kernel, as postulated by Lewis.[1]

Let me give a second example. By applying the proper corrections to a large number of intensities of x-ray reflection from a given crystal or crystal powder, taking the square root and using these structure factors (as they are called) as coefficients in a suitable Fourier Series, and then summing the series in the proper manner, it is possible in certain cases to obtain the time average distribution of scattering power (called, for short, the "electron density distribution") in a crystal.[2] Doing this for points along the center-line between adjacent atoms in the diamond, the curve shown in Fig. 1 has been obtained.[3] The small peak midway between the peaks representing the atoms of carbon is probably due to the electron pair serving as the bond holding the atoms together. In calcium fluoride we have found similar peaks, but before we can be sure of this interpretation it will be necessary to apply the method to a number of other crystals.

As a third example may be mentioned the evidence regarding atomic structures and interatomic forces which can be gained from a study of the relative distances between atoms in different structures. One can both compare the sizes of different kinds of atoms in similar environments and study the effect of different environments on the apparent size.

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Crystal structure studies also give interesting and important information regarding the arrangement of atoms in molecules and ions. Only one example will be given here.

Tetramethylammonium chloroplatinate has a structure in which the $N(CH_3)_4^+$ and the $PtCl_6^{--}$ ions are distributed as are the F^- and Ca^{++} ions in the CaF_2 structure. (See Fig. 3 of the following paper.) Each nitrogen is surrounded tetrahedrally by four equivalent carbon atoms and each platinum octahedrally by six equivalent chlorine atoms. This and results with other ammonium derivatives studied with x-rays show very definitely that the fifth valence of nitrogen represents an electron transfer, producing a positive and a negative ion rather than a shared pair of electrons.[5] The equivalence of the six chlorine atoms around the platinum shows that a secondary valence bond, once formed, is not different from a primary valence bond. A consideration of this and many other similar structures shows most conclusively that secondary valence can be completely accounted for by assuming that both electrons of a secondary valence bond originate in the same atom, while the two electrons of a primary valence bond came from different atoms.[6]

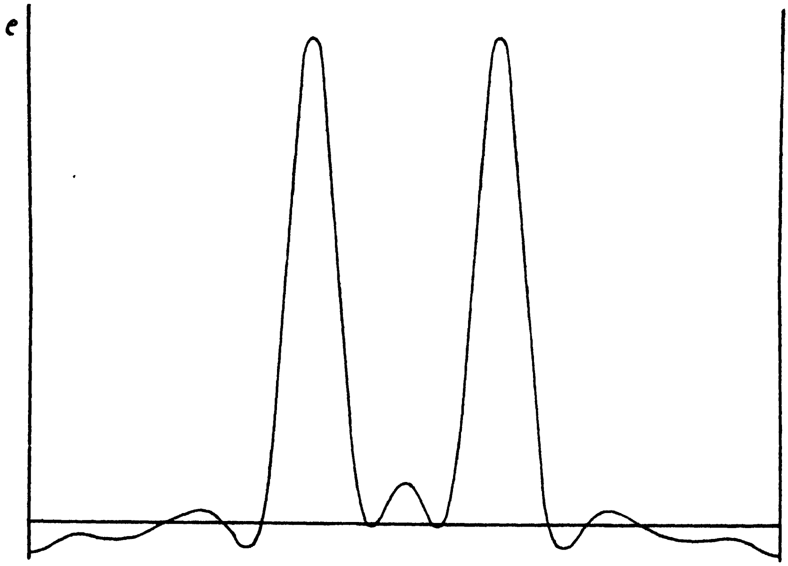

FIG. 1

The distribution of "electron density," as calculated from x-ray reflections, along the diagonal of the unit cube in the diamond. The large peaks show the positions of the carbon kernels.

By combining what is known about atoms and molecules from various other sources with the results of crystal structure analysis, one can now deduce certain basic principles governing the existence and stability of different types of arrangement, these principles accounting both for the empirical formulas of the compounds observed and for the actual arrangements of atoms in the structures.[7] Knowing these principles one can even predict with considerable success the structures of many crystals without experimental x-ray data.

The properties of solid matter depend to a large extent on just two things, —the structures of the component atoms and their arrangement in space. In the writer's opinion one of the most important aims of crystal structure analysis is the study of these relationships. Although little has been done along this line, much is possible. One can often relate brittleness and ready cleavage[8] to layer-like arrangements in which the distances between layers are relatively large and the forces between them weak, as indicated in Fig. 2, representing a two-dimensional crystal analogous to a crystal of arsenic, antimony or bismuth. Malleability and ductility can be attributed to the existence of "slip planes" (Fig. 3), the part of the crystal on one side of such a plane slipping readily with respect to the part on the other side.[9] The resulting arrangement, except on the surface, is exactly like that before the shift. Tensile strength and solubility can be readily interpreted, in simple cases at least, in terms of structure, especially when electrostatic potential theory is carefully applied. Optical properties (such as index of refraction) are also closely related to structure and the correlation has been studied in a few instances.

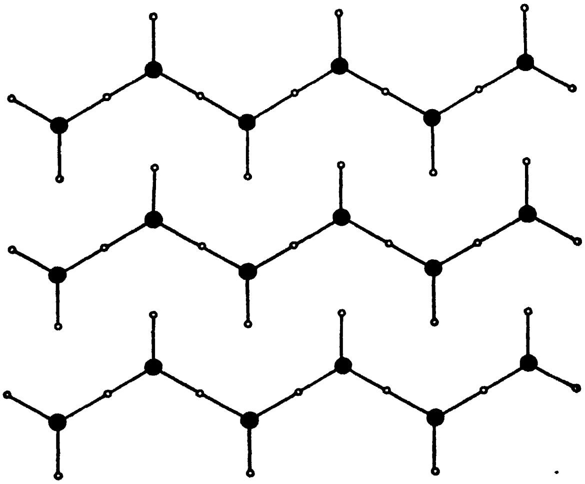

FIG. 2

A representation of a two-dimensional structure analogous to that of arsenic, antimony and bismuth.

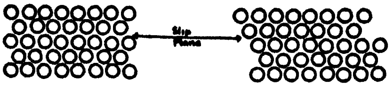

FIG. 3

Illustrating "slip planes." The interior of the crystal is the same after slipping as before.

The last few years have seen such a great development in methods and technique that it is now possible to study with success very complicated structures, provided one has the experimental facilities and knows the methods thoroughly. The theory of x-ray intensities is at last on a firm, satisfactory basis, making it possible to take full advantage of accurate, quantitative measurements. The results of the theory of space groups have been put in such form as to facilitate the analyses greatly; moreover, in cases in which a complete solution of the structure in terms of atomic positions is impossible, unimportant or too laborious, this theory frequently gives important information regarding the symmetry of the component atoms or molecules. Various graphical aids have been developed to simplify the process of interpreting the x-ray data. For example, the writer has made considerable use of a pivoted ruler, with which, from a rotating crystal photograph, one can readily make a projection and determine from that projection the size of the unit cell, the crystallographic indices of the reflections, and other useful information. Another rather new but extremely powerful aid to structure analysis is the method of calculating "electron densities" by Fourier Series summations,[2] already mentioned. A perhaps even more important development in crystal structure methods is the use, along with x-ray data, of principles and generalities derived from studies of known structures, considerations of potential theory, etc. For instance Professor W. L. Bragg has used the conception of close-packing of oxygens, considered as spheres, in working on the silicates; Pauling has made much use of coordination numbers (4 for silicon, 6 for aluminum, etc.) in similar work; while the writer has found the Lewis conception of valence very valuable in working out structures in which electronegative atoms are adjacent to each other. Considerations of the relative values of atomic dimensions, as obtained from other structures, are also frequently of great service.

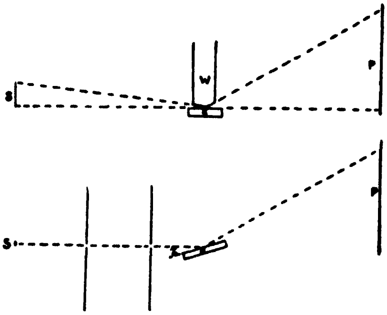

FIG. 4
Illustrating (upper) the Seemann wedge method and (lower) the oscillating crystal method of x-ray crystal photography. S = source of x-rays. C = crystal. W = wedge. P = photographic plate or film.

Before leaving the subject of crystal structures certain developments in apparatus should be noted. In particular, the progress made in high-vacuum technique makes feasible the use of demountable x-ray tubes with interchangeable targets and cathodes. The sample crystal or powder can now be placed within a few centimeters of a strong source of x-rays, with only a thin aluminum window and a slit system (if desired) between, thus shortening enormously the required time of exposure. By employing a "line focus" cathode giving an elongated focal spot, one can use a convergent beam, fixed crystal method (Fig. 4) due to Seemann[10] and obtain useful photographs, similar to oscillating crystal photographs, in a small fraction of a second. With this method the crystal gives many reflections at once during the whole time of exposure, while with the oscillating crystal method each reflection is taking place only a very small fraction of the time. An analogous method with powders, (Fig. 5) developed independently by Seemann[11] and by Bohlin,[12] cuts down the length of exposure required for that type of photograph to somewhat less than a minute, a great advance over the 6 to 48 hours required if sealed-up glass x-ray tubes and a narrow incident beam are used. This type of apparatus should also prove very useful in studying needle-like crystals and fibrous structures. In cutting down the time in this way one cuts down proportionately the difficulties due to a background of scattered radiation obscuring the fainter lines.

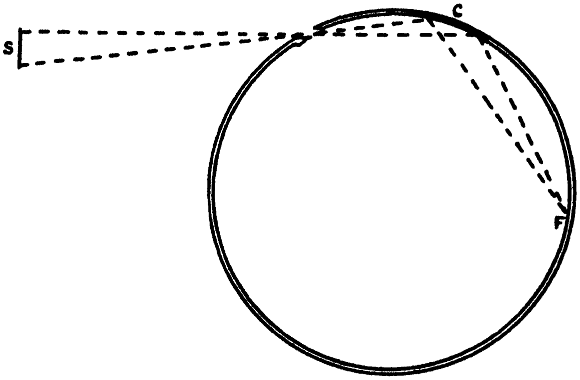

Fig. 5

Illustrating the Seemann-Bohlin method of x-ray powder photography. S = source of x-rays. C = crystal powder or metal foil. F = photographic film.

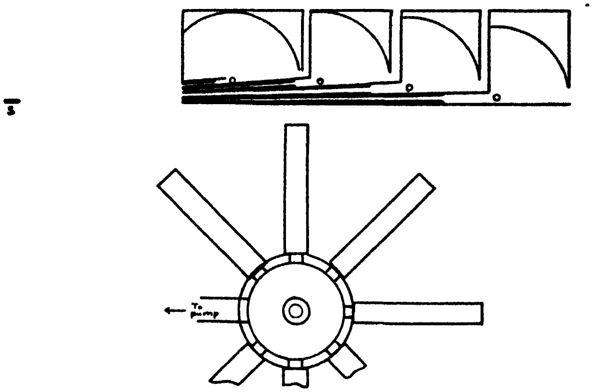

Fig. 6

(Upper) Cross-section of cassette for taking four x-ray photographs at once.
(Lower) Method of arranging seven such cassettes around a cylindrical x-ray tube, making it possible to take 28 photographs at once.

Another way of saving time is to use an x-ray tube and cameras designed to make possible a number of photographs at once. One scheme for doing this is diagrammatically shown in Fig. 6.

The interpretation of photographs obtained by reflection from a crystal or powder of the characterisitc radiation—of wave-lengths characteristic of the element composing the target—is complicated by the fact that this radiation is not strictly monochromatic. Besides the Kα_1 and Kα_2 lines (which are very close together and can usually be treated as a single line) there is a Kβ line of somewhat shorter wave-length,—much fainter, it is true, but still strong enough to increase considerably the difficulty of unambiguous interpretation of the photographs in some cases (See Fig. 7). A filter[13] containing an element of slightly lower atomic number than the element of the target will cut out most of the Kβ intensity without diminishing very greatly the intensity of the Kα lines. However, because there is still some of the β left to cause trouble by confusion with faint Kα reflections (often the most useful in certain parts of the structure analysis) and because of the diminution in intensity of the Kα lines, it is perhaps preferable merely to make identification of the Kβ lines certain by placing the filter over only half of the slit or half of the sample. The beta lines are then those half of which are very markedly stronger than the other half. Probably a still better way, because it cuts out both the beta radiation and the general or white radiation, is to reflect the x-rays first from a crystal of calcite or some other good reflector. By grinding the crystal so that the reflected rays just graze the surface a reflected beam practically as intense as a direct beam of the same cross-section can be obtained. (Fig. 8).

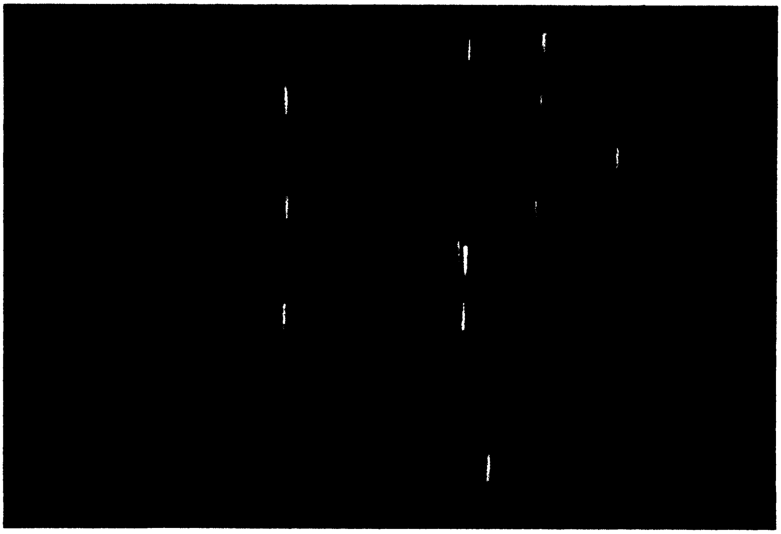

FIG. 7

An oscillating crystal x-ray photograph. Note that for nearly every strong reflection there is a fainter reflection slightly closer to the image of the undeflected beam. The former are the Kα, the latter the Kβ reflections from the same atomic planes in the crystal.

The assumption that the structure of the interior of a crystal extends in unmodified form to the crystal surfaces, although not strictly true, is at least approximately so and the nature and amount of the distortions can be estimated. One can then relate in a qualitative and semi-quantitative way the surface structure to rates of reaction, including the rates of growth and solution of the crystal, and to adsorption and catalysis. Experiments on these things, using crystals of known structure grown or cleaved under the proper conditions, would in the author's opinion be well worth doing, but so far as he knows none have yet been attempted. Another method of attack on surface problems is suggested by the fact that certain substances, such as urea, will, if dissolved in a solution from which sodium chloride is crystallizing, change the habit of the crystals, producing octahedra instead of cubes.[14] If methyl chloride, for instance, would do the same thing, one might reasonably assume the crystal surface to be a nearly monomolecular layer of methyl chloride molecules in a regular arrangement,—perhaps the same as the arrangement of chloride ions in a layer parallel to the surface—and all oriented in the same way,—with the methyl groups extending away from the crystal.[15] The use of such approximately known surfaces in catalysis experiments might to a large extent eliminate one of the usually unknown variables.

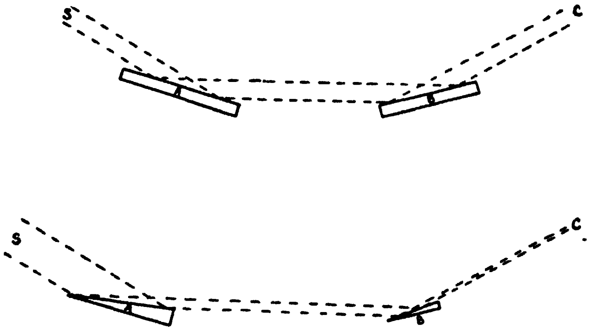

Fig. 8

Illustrating a method of obtaining a fairly intense monochromatic x-ray beam, using a broad incident beam reflected from a crystal ground so that the surface makes but a small angle with the reflected beam.

One very important field of x-ray research which has only begun to be explored[16] is that of studies of liquids and solutions. Diffraction effects are observed similar to those from crystal powders, but much more diffuse. There is some disagreement about the interpretation of the results obtained, but further experimental work will undoubtedly clear that up. What is most needed just now seems to be quantitative work using truly monochromatic x-rays and studying liquids or solutions of simple substances whose structures and interatomic distances are already quite accurately known from crystal structure or band spectra results. Studies of gases with x-rays[17] have been just sufficient to show that this is a most promising method of attack on some molecular structure problems. Complications due to intermolecular interference are negligible. The chief experimental difficulty is that of obtaining sufficient intensity, but there are ways of accomplishing that.

Other promising fields of x-ray work are studies of liquid crystals, in which there is probably only one- or two-dimensional regularity; studies of fibers, which may be considered as aggregates of needle-like crystals with their long axes approximately parallel but with random orientation otherwise; studies of particle size, from the width of spectrum lines; studies of the effect of mechanical and heat treatment or impurities on type of structure, distortions, particle size, etc. In this connection, phase rule studies using x-rays seem to give more definite results than other methods and with suitable refinements of technique they can be carried out with greater speed. With suitable equipment x-ray studies at low and high temperatures can readily be made and for such problems as those just mentioned are of inestimable value.

The study of photochemical reactions produced by x-rays might increase considerably our knowledge of such fundamental processes.[18] A monochromatic source of fairly high intensity and a method for measuring the absolute amount of energy absorbed are the chief requirements, and these can be met without much trouble.

The use of x-rays for qualitative and quantitative analysis will next be considered. One can analyze either for the chemical elememts present or for particular compounds. Analyzing for compounds is usually done by obtaining x-ray photographs of powders just as if one were to attempt a structure analysis. Each crystalline species,—compound or free element,—is identified by means of a characteristic set of lines on the photograph, a mixture giving the lines corresponding to all the types of crystal present. It is usually necessary to have a similar photograph of a pure sample of each compound (or free element) being looked for. The presence of a set of lines in the correct relative positions and with the correct relative intensities is practically proof of the presence of the corresponding compound, but the method as at present carried out is not very sensitive to small amounts of impurities; nor is more than a rough quantitative analysis possible without comparison photographs of knowns of similar composition. By using Seemann-Bohlin focussing cameras or by designing camera and x-ray tube so as to take a number of photographs at once, with the samples as close as possible to the source of x-rays, the time element can be largely eliminated. Another difficulty in the case of complex mixtures is removed if one either labels or eliminates entirely the $K\beta$ radiation by one of the methods which have been suggested, thus effectively halving the complexity of the photograph being studied.

In analyzing for elements[19] one can place the sample to be studied either (a) on the target of the x-ray tube, studying the primary emission spectra, (b) near the cathode within the tube, studying the secondary or fluorescent emission spectra or outside of the tube, studying either (c) the secondary emission spectra or (d) the absorption spectra. The most sensitive method is the first, 1 part in 10^6 or 10^7 being detectable in favorable cases.[20] It has the disadvantages that a volatile sample cannot be used and that quantitative estimates are quite unreliable, except in certain specific cases as when the spectra of metals of nearly equal atomic number are excited under equivalent conditions.[21] Both first and second methods are unsuited for rapid analyses, as the x-ray tube must be taken apart, breaking the vacuum, to change the sample. The second and third methods require exposures of considerable duration, for the fluorescent radiation is relatively weak; nor are the results quantitatively very accurate, (although more accurate than those obtained by the first method[22]), unless one takes blanks at the same time or under identical conditions with knowns of similar composition. The last method mentioned[23] seems to the author most favorable for rapid, quantitative analysis. For many analyses one could use a fixed crystal, convergent beam method, cutting the exposure time per analysis probably to a minute or two. What are measured are the different positions of the absorption limits in the spectra, to get the kinds of elements present in the sample, and the relative intensities on the two sides of each absorption limit, to get the amount of each element in the path of the beam. Densitometer measurements of photographs can be used, or, what would perhaps be a more accurate method, the x-ray intensity differences could be measured with the aid of an ionization chamber-electrometer outfit. One might expect to get accuracies of a fraction of a per cent in this way, using suitable blanks and comparison standards. Without using a vacuum spectrograph this method is suitable for all elements having atomic numbers greater than about 24 (chromium) or 25 (manganese). With vacuum apparatus one can analyze for somewhat lighter elements, at least down to silicon, atomic number 14. There seems to be little hope at present of easy, accurate x-ray analysis for such light elements as carbon, nitrogen or oxygen, but x-ray methods bid fair to replace all others before long in analysis for the heavier elements.

The wave-length and so the position in the spectrum of the x-ray absorption limit of an element placed in the path of a beam of x-rays depends but little on the state of chemical combination of that element, for the wave-length is determined by the energy necessary to remove an electron from one of the inner electron shells in the atom and this is little affected by the number or arrangement of surrounding atoms. Studies with a vacuum spectrograph of the K absorption limits for such elements as phosphorus, sulfur or chlorine, however, show slight differences for different compounds.[24] For instance, all chlorides have practically the same limit; all chlorates have nearly the same limit (but a different one from that for chlorides); perchlorates are still different, etc. If one could increase the resolving power somewhat it would be possible to measure significant differences between different chlorine compounds within each class, thus obtaining an experimental measure of the electropositiveness or electronegativeness of the atom attached to the chlorine. Using organic compounds one could thus classify various radicals according to their pull on the electron pair bonding them to chlorine,—a most useful series in organic chemistry. Also one could take an unknown and determine not only whether or not it contains chlorine but the nature of the atom or group to which the chlorine is attached. Similarly for sulfur and phosphorus and some other elements. The effect of change of state, solvation and adsorption on the wave-lengths would also make most interesting studies.

Greater resolving power without loss of intensity can be obtained by reflecting the x-rays from two crystals,[25] set up as shown in Fig. 9, A broad incident beam is used. Crystal A remains fixed in position while crystal B is rotated, different positions of B sending different wave-lengths into an ionization chamber at C. Only one wave-length will be reflected by both crystals in a given pair of positions. Others, if reflected by A, will not strike B at the proper angle for reflection. Ross has suggested using a *horizontal* slit at S and putting a photographic plate at C. With both crystals fixed in position, different *heights* at C would then represent very slightly different wave-lengths. Such a scheme could be made more sensitive to weak radiations by grinding the crystals so as to concentrate all of the doubly reflected rays into a narrow beam. An arrangement of this sort in vacuum would greatly improve the sensitivity of absorption edge measurements and in all probability would make possible such distinctions between different compounds as mentioned above.

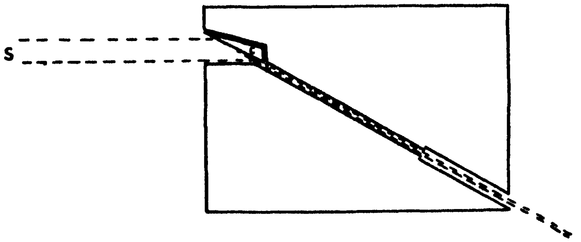

FIG. 9
Illustrating double crystal reflection, with and without the crystal surfaces ground nearly parallel to the reflected beam.

In the foregoing, reference has been made chiefly to photographic methods of obtaining data, but it should be mentioned that with good equipment and technique it is possible to observe many diffraction effects *visually* on a fluorescent screen. When the best conditions have been found, it is quite possible that visual observations will prove of great value, for instance in analyzing for elements of compounds and in following structural changes accompanying thermal or mechanical treatment.

In conclusion the writer wishes to emphasize the fact that although enough has been done along the various lines mentioned to indicate in a general way what are the possibilities and limitations of this new scientific tool, the best design of apparatus for each purpose, the best conditions of operation, etc., will be known only after more research.

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References

[1] G. N. Lewis: "Valence and the Structure of Atoms and Molecules," (1923).

[2] W. H. Bragg: Phil. Trans., **215A**, 253 (1915); Epstein and Ehrenfest: Proc. Nat. Acad. Sci., **10**, 133 (1924); Duane: Proc. Nat. Acad. Sci., **11**, 489 (1925); Havighurst: Proc. Nat. Acad. Sci., **11**, 502, 507 (1925); W. L. Bragg: Proc. Roy. Soc., **123A**, 537 (1929).

[3] Huggins and Parrish: Phys. Rev. (2) **35**, 136 (1930); Parrish: Thesis for the degree of Master of Arts, Stanford University, 1930.

[4] Huggins: Phys. Rev., (2) **27**, 638 (1926).

[5] Lewis: Ref. 1.

[6] Huggins: J. Phys. Chem., **26**, 601 (1922).

[7] Cf. the following paper; also Pauling: J. Am. Chem. Soc., **51**, 1010 (1929).

[8] Huggins: Am. J. Sci., **5**, 303 (1923).

[9] Cf. Jeffries and Archer: Chem. Met. Eng. **24**, 1057 (1921); "The Science of Metals," (1924).

[10] Seemann: Ann. Physik, **49**, 470; **51**, 391 (1916); Physik. Z., **18**, 242 (1917); **20**, 51 (1919); Naturwissenschaften, **17**, 960 (1929).

[11] Seemann: Ann. Physik, **59**, 455 (1919).

[12] Bohlin: Ann. Physik, **61**, 421 (1920).

[13] Hull: Phys. Rev., (2) **10**, 661 (1917).

[14] Retgers: Z. physik. Chem., **9**, 267 (1892); Saylor: J. Phys. Chem., **32**, 1441 (1928).

[15] Mark: "Die Verwendung der Röntgenstrahlen in Chemie und Technik," 302 (1926).

[16] Stewart and Co-workers: Phys. Rev., (1927-30); Stewart: Chem. Rev., **6**, 483 (1929).

[17] Barrett: Phys. Rev., (2) **32**, 22 (1928); A. H. Compton: **35**, 925 (1930); Debye, Bewilogua and Ehrhardt: Physik. Z., **30**, 84 (1929).

[18] See, for instance, Glocker and Risse: Z. Physik, **48**, 845 (1928).

[19] Glocker: "Materialprüfung mit Röntgenstrahlen" (1927); Mark: Ref. 15, p. 200.

[20] Eddy, Laby and Turner: Proc. Roy. Soc., **124A**, 249 (1929); Laby and Eddy: Nature, **125**, 524 (1930).

[21] Eddy and Laby: Proc. Roy. Soc., **127A**, 20 (1930).

[22] Glocker and Schreiber: Ann. Physik, **85**, 1089 (1928); Schreiber: Z. Physik, **58**, 619 (1929); Hevesy, Böhm and Faessler: **63**, 74 (1930).

[23] Cf. Glocker and Frohnmayer: Ann. Physik, **76**, 369 (1925).

[24] International Critical Tables, VI, 44; Siegbahn: "Spectroscopy of X-rays," 142 (1925).

[25] Ehrenberg and Mark: Z. Physik, **42**, 807 (1927); Davis and Purks: Proc. Nat. Acad. Sci., **13**, 419 (1927); **14**, 172 (1928); Phys. Rev., (2) **32**, 336 (1928).

A CONDUCTIVITY METHOD FOR THE ANALYSIS OF BINARY MIXTURES OF THE VOLATILE FATTY ACIDS*

BY ELLIS I. FULMER, E. E. MOORE AND R. L. FOSTER

Practically all of the methods for the analysis of mixtures of the volatile fatty acids are based upon separation by distillation, that is they are modifications of the original Duclaux procedure. The various methods for the analysis of these compounds were reviewed by Moore and Fulmer[1] who proposed a method for the analysis of mixtures of formic and acetic acids based upon a conductometric titration with ammonium hydroxide. Werkman[2] has developed a procedure based upon the distribution of the acids between water and an immiscible solvent.

In the paper here presented are given data leading to a simple conductivity procedure for the analysis of binary mixtures of the volatile fatty acids a preliminary report of which was made by Moore, Fulmer and Foster.[3]

Procedure

The equipment used consisted of a Vreeland Oscillator, Kohlrausch bridge and telephone receiver with standard adjuncts. The apparatus was appropriately shielded. The Washburn pipette type of cell was used. The cell constant was determined by the use of KCl solutions at the same ranges of specific conductivities as the solutions to be tested. The cell constant was likewise determined for the various bridge readings, a necessary precaution as emphasized by Wark.[4] The conductivities were measured at 25°.

The acids were the purest obtainable on the market and were redistilled, the middle fractions only being used in the preparation of the standard solutions.[5,6]

Experimental Results

The data for the specific conductivities for 0.0100 N solutions of formic-acetic, formic-propionic, formic-n-butyric, and acetic-propionic acids are given in Table I.

Discussion of Results

The specific conductivity of the mixtures is obviously not a linear function of the percentage composition. However, the antilogarithm of $10^3\times$ specific conductivity is a linear function, within reasonable limits for analytical purposes, of the percentage composition, or if,

S'_{AB} = Antilogarithm of $10^3\times$ specific conductivity of mixture of acids A and B at a given normality.

S'_A = Antilogarithm of $10^3\times$ specific conductivity of acid A at the same normality as the mixture.

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* A Contribution from the Laboratory of Biophysical Chemistry, Iowa State College, Ames, Iowa.

TABLE I

Specific Conductivities of Binary Mixtures of Formic, Acetic, Propionic and Butyric Acids at 0.01 N.

C_A = % of first acid in mixture; S_{AB} = specific conductivity × 10^3;

S' = antilogs

C_A	Formic-Acetic				Formic-Propionic			
	C_A (calc.)	% diff.	S_{AB}	S'	C_A (calc.)	% diff.	S_{AB}	S'
0	0.01	+0.01	0.1579	1.4380	−0.05	−0.05	0.1366	1.3698
20.00	19.52	−0.48	0.2477	1.7688	18.91	−1.09	0.2321	1.7067
33.33	—	—	—	—	—	—	—	—
40.00	40.27	+0.27	0.3625	2.1028	40.39	+0.39	0.3198	2.0884
50.00	—	—	—	—	—	—	—	—
60.00	60.70	+0.70	0.3923	2.4673	61.77	+1.77	0.3859	2.4683
66.67	—	—	—	—	—	—	—	—
80.00	79.67	−0.33	0.4456	2.7891	79.71	−0.29	0.4437	2.7902
100.00	99.84	−0.16	0.4960	3.1311	99.08	−0.92	0.4960	3.1311

Formic-Acetic:

$$S' = 0.01696\,C_A + 1.4378$$

$$C_A = \frac{S'_{AB} - 1.4378}{3.1338 - 1.4378} \times 100$$

Av. % diff. = +0.0017

Formic-Propionic:

$$S' = 0.01776\,C_A + 1.3707$$

$$C_A = \frac{S'_{AB} - 1.3707}{3.1474 - 1.3707} \times 100$$

Av. % diff. = −0.05

TABLE I (continued)

C_A	Formic-Butyric				Acetic-Propionic			
	C_A (calc.)	% diff.	S_{AB}	S'	C_A (calc.)	% diff.	S_{AB}	S'
0	−0.90	−0.90	0.1447	1.3985	+1.15	+1.15	0.1366	1.3698
20.00	—	—	—	—	19.04	−0.96	0.1405	1.3822
33.33	33.42	+0.09	0.2971	1.9880	—	—	—	—
40.00	—	—	—	—	40.11	+0.11	0.1451	1.3968
50.00	49.67	−0.33	0.3556	2.2684	—	—	—	—
60.00	—	—	—	—	60.89	−0.89	0.1496	1.4112
66.67	66.60	−0.07	0.4086	2.5604	—	—	—	—
80.00	—	—	—	—	79.53	−0.47	0.1539	1.4254
100.00	99.91	−0.09	0.4960	3.1311	99.56	−0.44	0.1579	1.4380

Formic-Butyric:

$$S' = 0.01725\, C_A + 1.4114$$

$$C_A = \frac{S'_{AB} - 1.4114}{3.1366 - 1.4114} \times 100$$

Av. % diff. = −0.256

Acetic-Propionic:

$$S' = 0.0006985\, C_A + 1.36906$$

$$C_A = \frac{S'_{AB} - 1.36906}{1.4383 - 1.36906} \times 100$$

Av. % diff. = +0.047

S'_B = Antilogarithm of $10^3 \times$ specific conductivity of acid *B* at the same normality as the mixture.

C_A and C_B = percent of each acid present at the given normality.

$$C_A + C_B = 100$$

$$(1) \quad S'_{AB} = mC_A + S'_B$$

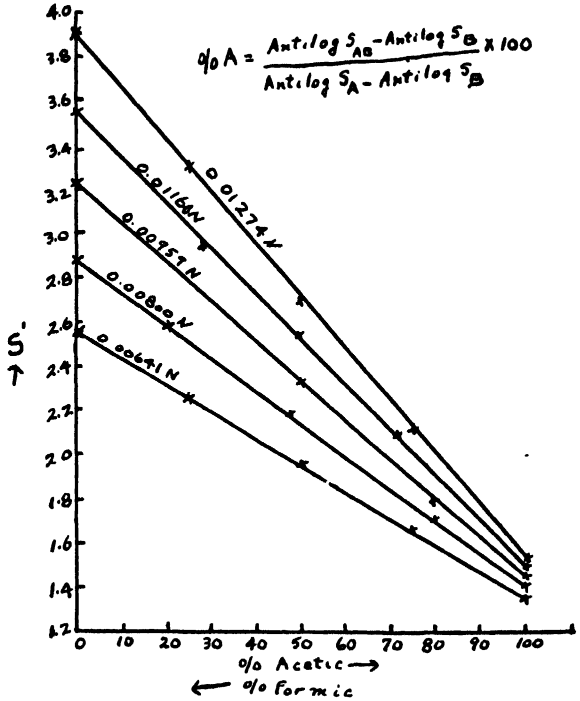

FIG. 1

and

$$(2) \quad S'_{AB} = \frac{(S'_A - S'_B)\, C_A}{100} + S'_B$$

and

$$(3) \quad C_A = \frac{S'_{AB} - S'_B}{S'_A - S'_B} \times 100$$

In the table the equations for the various mixtures are given as calculated by the method of least squares permitting the establishment of standard values for S'_A and S'_B. Calculated values are also given for C_A for each mixture. The linear relation between the antilogarithm of $10^3 \times$ specific conductivity and the percentage composition was found to hold for mixtures of formic and acetic acids for the following normalities, 0.00641 N, 0.00800 N, 0.00959 N, 0.0116 N and 0.0127 N. These data are graphed on Fig. 1.

Summary

It has been shown that the antilogarithms of $10^3\times$ specific conductivities of binary mixtures of formic, acetic, propionic, and n-butyric acids are a linear function of the percent composition of the solutions. The above relation is proposed as a basis for the analysis of such binary mixtures.

References

[1] E. E. Moore, with E. I. Fulmer: Iowa State Coll. J. Sci., **4**, 1-25 (1929).
[2] C. H. Werkman: Ind. Eng. Chem. Analytical Ed., **2**, 302 (1930).
[3] E. E. Moore, E. I. Fulmer and R. L. Foster: J. Bact., **19**, 5 (1930).
[4] I. W. Wark: J. Phys. Chem., **34**, 885-6 (1930).
[5] W. Ostwald: Z. physik. Chem., **3**, 170-197 (1889).
[6] J. Kendall: J. Am. Chem. Soc., **39**, 7-24 (1917).

THE SYSTEM P_2O_5–CaO–H_2O AND THE RECRYSTALLIZATION OF MONOCALCIUM PHOSPHATE*

BY NORMAN ASHWELL CLARK

Primary or monocalcium phosphate is employed to a considerable extent in nutrient media; it is of general use for the growth of green plants in inorganic solutions[1] and is specified for solutions numbers 3 and 4 in the plan for cooperative research of the National Research Council.[2] The salt is frequently referred to as the soluble calcium phosphate, and is of interest from the standpoint of soils in that it is the chief component of the commercial 'acid phosphate' fertilizers. The behavior of the salt in solution and its purity when used in experiments are therefore of more than usual importance.

Small quantities of water readily decompose monocalcium phosphate. Stoklasa[3] gives one part of salt to 200 parts of water for solution without decomposition. He states further that the pure salt decomposes very slowly in a closed vessel, setting free H_3PO_4. Cameron and Seidell[4] also found a considerable amount of free acid in a sample of Kahlbaum's manufacture, and they pointed out that it is impracticable to obtain the monocalcium phosphate without an excess of acid.

Because of this decomposition by water, it is necessary to recrystallize from acid solution in order to purify the salt, but the optimum conditions for precipitation set out in the literature are indefinite. Abegg's Handbuch[5] states that the monocalcium phosphate crystallizes by evaporation of strongly acid solutions of the other calcium phosphates. Stoklasa used 31 per cent H_3PO_4 and dicalcium phosphate to obtain the primary salt. Pointet[6] investigated the commercial monocalcium phosphate and found a very large excess of acid in the amorphous salt. He suggested pressing out some of the acid or adding dibasic calcium phosphate to the solution to produce crystallization—an indication that too great a concentration of acid might prevent precipitation of the salt. Causse[7] reported that if he added di- or tricalcium phosphate with more than 30 grams of H_3PO_4 in 100 cc. the mono salt precipitated. Prunier and Jouve[8] placed a mixture of phosphoric acid and dicalcium phosphate in molecular proportions in a quantity of water equal to the weight of the two (approximately 30 per cent acid) and found that by rapid evaporation they obtained dicalcium phosphate or a mixture of this with mono phosphate, but by very slow evaporation the mono salt precipitated.

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* Contribution from the Department of Chemistry, Iowa State College.

[1] Clark: J. Phys. Chem., **29**, 935 (1925).

[2] Livingston: Plan for cooperative research. Johns Hopkins Univ. (1919).

[3] Listy Chem. **13**, Abstracted in J. Chem. Soc., **58**, 695 (1890).

[4] J. Am. Chem. Soc., **26**, 1454 (1904).

[5] "Handbuch anorg. Chemie", **2** II, 151 (1905).

[6] Bull., (3) **5**, 254 (1891).

[7] Compt. rend., **114**, 414 (1892).

[8] J. Pharm. Chim., (6) **10**, 529 (1899).

Cameron and Seidell in 1904[4] and in 1905[9] made the first systematic attempt to clear up the difficulties. They determined the isotherm at 25 C. for the system P_2O_5-CaO-H_2O and at a concentration of 77 grams CaO and 317 grams P_2O_5 per liter found both the solid phases, monocalcium phosphate and dicalcium phosphate, in equilibrium with the solution. They also noted that there was a region of meta-stable equilibrium for the monocalcium phosphate where that salt would exist in contact with a solution containing less P_2O_5 than required by the triple point, until agitation, standing or rise of temperature caused the precipitation of the dicalcium phosphate.

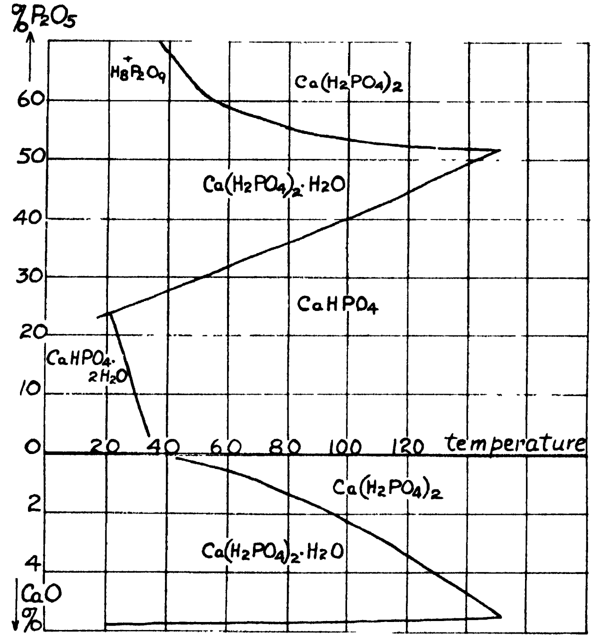

Fig. 1

Projection of part of space model of the system CaO-P_2O_5-H_2O. (After Bassett).

H. Bassett in 1908[10] made an extensive study of the system CaO-P_2O_5-H_2O in order to get the main points of the space model. He determined the isotherms at 50.7°, 40° and 25°, and fixed a number of the quintuple points. Fig. 1 is a projection of part of this model and shows the area for $Ca(H_2PO_4)_2 \cdot H_2O$.

When these isotherms are plotted with an amount of water which is constant over the diagram, it is possible to draw further conclusions as to the

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[9] J. Am. Chem. Soc., **27**, 1503 (1905).

[10] Z. anorg. Chem., **59**, 1 (1908).

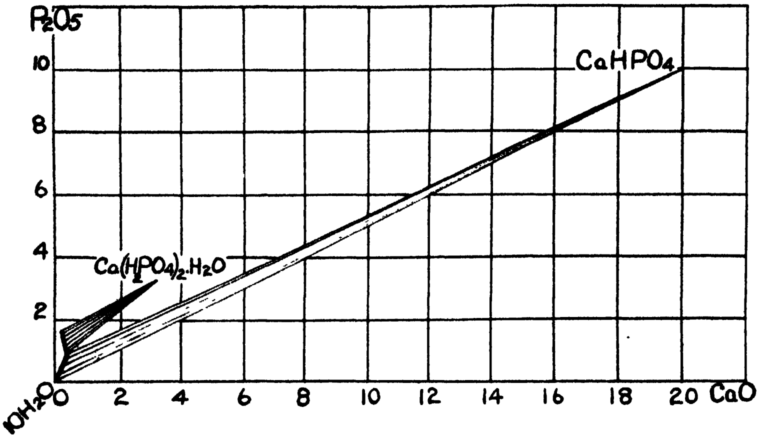

FIG. 2

Isotherm at 100° showing position of CaHPO₄ and Ca(H₂PO₄)₂.H₂O. Quantities in moles. 10H₂O over diagram.

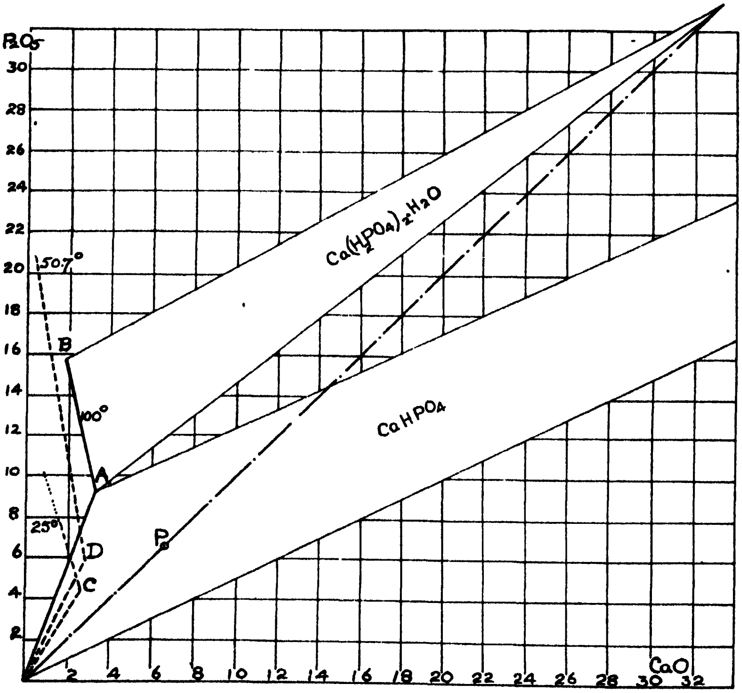

FIG. 3

Isotherms at 100°, 50.7°, and 25°. Quantities in moles. 100 H₂O over diagram.

behavior of the system. Fig. 2 shows the approximate position of the isotherm at 100°, the position of the monocalcium phosphate with one H_2O and that of the anhydrous dicalcium phosphate, and has 10 moles of water over the diagram. The 'tie-lines' join the salts to the isotherm. Fig. 3 gives the same points but is on a larger scale with 100 moles of water. The dotted lines show the isotherms for 50.7° and 25°. On these scales the curves can be represented as straight lines which would intersect at the origin if no other phases existed.

An examination of these figures indicates the limits of the triangles within which there is equilibrium between one of the solid phases and a solution on the isotherm. For systems at 100° a solution within the triangle bounded by that isotherm and $Ca(H_2PO_4)_2.H_2O$ is unstable and will precipitate that salt, while solutions within the triangle bounded by the isotherm and $CaHPO_4$ will precipitate the dicalcium phosphate. It will be seen that both curves lie outside the triangle formed by H_2O at the origin and the points marked $Ca(H_2PO_4)_2.H_2O$ and $CaHPO_4$ (Fig. 2); that is, the solution at A (Fig. 3) is incongruent[11] and with $CaHPO_4$ can form water and $Ca(H_2PO_4)_2.H_2O$, or if A is evaporated at 100° in the presence of the dicalcium phosphate, that salt will dissolve and the monocalcium phosphate will precipitate, while the composition of the solution remains as at A until all the dicalcium salt has disappeared. If no dicalcium phosphate is present and the solution represented at A is evaporated at 100°, monocalcium salt precipitates and the solution increases in P_2O_5 content, the successive compositions being represented by the points on the isotherm. At B both the hydrated and dehydrated monocalcium phosphates are in equilibrium with the solution.

A solution of composition represented by the point A was made up of 25.2 per cent of the recrystallized monocalcium phosphate, 35.6 per cent of H_3PO_4 crystals prepared from the acid solution by the method outlined by Ross[12] and by Clark[13] centrifuged in glass containers and dried over P_2O_5, and 39.2 per cent of water. The clear solution was evaporated in an oven at 100° with the beaker almost covered. This caused the crystals to be formed under the liquid; if evaporated without the cover the crystals form on the surface as a skin and may fall or may need to be pushed to the bottom. After crystallization has proceeded for some time the liquid was poured off into weighing bottles and analysed.

The method adopted for analysis of calcium was that studied by McCrudden[14] and recommended for use when phosphorus is present. The calcium was weighed as CaO. For phosphorus, the Bureau of Standards 'Standard' method of double precipitation with magnesia mixture[15] was found excellent. The analyses reported are the average of two closely agreeing determinations.

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[11] Meyerhoffer: Ber., **30**, 1804 (1897).

[12] Ind. Eng. Chem., **17**, 1081 (1925).

[13] Proc. First Int. Cong. Soil Sci., **3**, 300 (1927).

[14] J. Biol. Chem., **10**, 187 (1911).

[15] Epperson: J. Am. Chem. Soc., **50**, 321 (1928).

The composition of the solution after separation from the crystals was 43.12 per cent P_2O_5 and 5.12 per cent CaO. This is 10.5 moles P_2O_5, 3.2 CaO and 100 H_2O, and the point falls almost on the isotherm as drawn.

A solution given by the point D is in equilibrium with both the mono and dicalcium salts at 50.7°. If evaporated at 50.7° $Ca(H_2PO_4)_2 . H_2O$ is precipitated and the solutions obtained are represented by the dotted isotherm (Fig. 3). If evaporated at a higher temperature (e.g. 100°) it can be seen from the figure that the solution at D will precipitate the dicalcium salt at first and its concentration will reach the point A. On the other hand if the solution at D is cooled, it falls within the mono salt area and $Ca(H_2PO_4)_2 . H_2O$ is precipitated.

A solution was made up of 23.5 per cent of recrystallized monocalcium phosphate, 23.7 per cent H_3PO_4 crystals and 52.8 per cent water, which is approximately the concentration at the point D. It was then evaporated at 50°-51° while slowly stirring. Crystallization started in 45 minutes and after 7 hours a sample was filtered through a jacketed funnel and analysed after rejecting the first few cc of the filtrate. The liquid contained 5.00 per cent CaO and 35.4 per cent P_2O_5 which corresponds to 2.7 moles CaO, 7.6 moles P_2O_5 and 100 H_2O, a point which is almost on the isotherm. After further evaporation the solution was again analysed and found to contain 2.5 CaO, 8.3 P_2O_5 and 100 H_2O, which falls on the curve.

The point P represents 30 per cent P_2O_5 and 12 per cent CaO. This is the composition of one of the mixtures of Prunier and Jouve[8], and it is clear that at 100° there is equilibrium in the system between the dicalcium solid phase and a solution on the isotherm. We should expect, therefore, that boiling, violent shaking or long standing would cause the dicalcium phosphate to precipitate —as Prunier and Jouve found actually occurred through quick evaporation. Very slow evaporation, however, gave them the monocalcium phosphate. This salt would be formed as soon as the composition of the solution reached A, where any dicalcium phosphate which had solidified would tend to dissolve and the monocalcium to precipitate. The farther the evaporation was carried the more monocalcium phosphate would result. As the point P is on the line joining the origin to the $Ca(H_2PO_4)_2 . H_2O$, there would always be a trace of $CaHPO_4$ present. When the point giving the composition used falls to the left of the dotted line, theoretically all the dicalcium phosphate should dissolve, but practically it is almost impossible to obtain this because of the slowness with which the dicalcium phosphate reacts in a matrix of primary crystals. This will be referred to later.

A solution with composition represented at C (Fig. 3), when evaporated at 25° produces the mono salt, while the solution increases in concentration of the P_2O_5. Birnbaum[16] obtained crystals without raising the temperature by drying over concentrated sulphuric acid. Neither Cameron nor Bassett determined exactly how far the 25° isotherm should be carried, and that corner of the space model has yet to be investigated, but it can be seen from Fig. 1 that the solution does not come into equilibrium with the anhydrous monophosphate as it would if evaporated at 100°.

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[16] Z. Chem., 1871; Gmelin-Kraut: "Handbuch", 2 II, 302 (1909).

A solution of the composition at C, when tested by evaporation over concentrated sulphuric crystallized very slowly—after some three weeks over the acid at room temperature (near 25°) the composition of the solution centrifuged from the crystals was 1.5 moles CaO, 7.8 P_2O_5 and 100 H_2O, which lies near the 25° curve. A series was also run at room temperature over concentrated sulphuric with from 33 to 40 grams of the salt per 100 cc of acid, 15 to 18 per cent H_3PO_4, giving concentrations near the point C; ten days elapsed before crystallization commenced and for some weeks the crystallization continued. The time required might be somewhat shortened but as a method of recrystallization it is very slow.

A quicker way to purify the monocalcium phosphate is to make up a solution at 100°, evaporate at that temperature or slightly below until crystallization is well started, (it is advisable to prevent the crystals forming a thick layer on the surface), then to cool to 50° and to centrifuge; the amount of acid originally present in the solution may vary within limits, but it will be seen from the curves that there is no point in making the acid concentration very small as it will increase to A or beyond. The composition of the original system must not fall to the right of the line joining the origin to $Ca(H_2PO_4)_2.H_2O$ (Fig. 3), as the system would then precipitate more $CaHPO_4$ than would dissolve; the solution at A would dry up and leave a mixture of the two salts.

A similar mixture of the two salts may be formed if the composition of the system to be evaporated falls to the left of the line joining the origin to $Ca(H_2PO_4)_2.H_2O$ but within the $CaHPO_4$ triangle. Here the dicalcium salt precipitates first, but should dissolve when the solution concentration reaches A and pure monophosphate result. Even with regular stirring it seems to be difficult to remove all the dicalcium salt, and if the solution is left to evaporate undisturbed, most of the dicalcium fails to dissolve and the two forms of crystals will exist together for a long period of time.

This slowness in attaining equilibrium was commented upon both by Cameron and Seidell and by Bassett. The theoretical percentages of P_2O_5 and CaO in the monocalcium phosphate are 56.35 and 22.22; Bassett[10] reported usually a high CaO content, a condition he attributed to the presence of small amounts of $CaHPO_4$ in the crystals. In this laboratory, systems with a concentration near point C, even when evaporated with stirring at 100° have shown this high CaO content, which tends to confirm Bassett's explanation, although no traces of the dicalcium salt could be seen.

Solutions with concentrations which fall within the triangle made by the origin and the isotherm AB, when evaporated at 100°, will be clear of the dicalcium phosphate and will precipitate the primary salt; for recrystallization, therefore, it is better to have the system fall within these limits. Crystals produced in this way and analysed after centrifuging did not show a high CaO content; the ratio of P_2O_5 to CaO was slightly higher than the theoretical. This increase in the P_2O_5 may have been due to the presence of some of the acid from which the crystals were not completely separated. Similarly, crystals obtained at 25°, by evaporation over sulphuric acid, showed a ratio of P_2O_5 to CaO a fraction higher than theoretical but lower than those from evaporation at 100°, and as these were produced in a lower concentration of acid, this smaller ratio would tend to support that conclusion.

Two precautions are necessary when crystals are obtained by evaporating solutions whose composition falls within the triangle formed by the origin and the isotherm AB. If the air above the solution is much cooler than the solution itself, crystals form on the surface as a skin and may persist there giving rise to local conditions which cause white spots to appear. This can be prevented by pushing the crystals below the surface or by evaporating in an oven at 100°. Secondly, if the solution is suddenly chilled when it has a concentration near the 100° isotherm, a voluminous white precipitate forms which is exceedingly soluble in water and very difficult to separate from the solution. Slow cooling to 50° prevents the appearance of this precipitate. It is a simple matter to make up a solution represented by the point A, or with slightly more water and acid, evaporate until 10 to 20 per cent of the total weight is lost (crystallization will be well started), cool slowly to 50° and centrifuge.

By the use of recrystallized phosphoric acid a very pure sample of monophosphate can be prepared by recrystallizing the primary calcium salt as described above. It is difficult to remove every trace of excess H_3PO_4 from the crystals. Stoklasa[3] suggested removing the excess acid by washing with alcohol and ether. Samples treated in this way should be used with caution, as some gave a strong tarry odor after a few weeks in stoppered bottles, and there was also some indications that water of crystallization had been removed. The exact theoretical content of water of crystallization was not attained and this is being further investigated, but crystals without the excess of CaO can be produced quickly by the method outlined.

Summary

1. An examination has been made of parts of the space model for the system CaO-P_2O_5-H_2O as drawn by Bassett, and the indicated behavior of mono and dicalcium phosphates in solution has been investigated.

2. Methods for the recrystallization of the monocalcium phosphate have been given.

THE REDUCTION OF NITRIC OXIDE*

BY M. L. NICHOLS AND C. W. MORSE

A theory for the mechanism of the reduction of nitric acid has been proposed and developed in previous papers[1] from this laboratory. These studies required a knowledge of the reactions between the reducing agents and the reduced nitrogen compounds formed from the acid. In the case of nitric oxide the published results[2] were only qualitative and often contradictory. The purpose of the present investigation was the quantitative determination of the effect upon the reduction products of nitric oxide caused by the variation of the temperature, the acidity, and the concentration of some strong reducing agents.

Experimental

Quantitative Experiments

The methods for the preparation and the analysis of the reagents and the reduction products used in this work were those described in detail by Milligan.[3] A brief outline of these methods is given below and any deviation from Milligan's procedure is described.

Nitric Oxide. The nitric oxide was prepared by the action of 2 cc. of dilute nitric acid and 15 cc. of concentrated sulphuric acid upon the mercury in the nitrometer, A, Fig. 1.

The nitric oxide content of the gas mixtures was determined by measuring the decrease in volume that resulted from the treatment of the gas with two 25 cc. portions of a mixture of 2 cc. of concentrated nitric acid with 100 cc. of concentrated sulphuric acid. It was found that 25 cc. of this acid mixture would completely dissolve 100 cc. of pure nitric oxide and that no gas could be pumped from this solution. In the apparatus used by Milligan it was not possible to measure the decrease in volume directly and the nitrosylsulfuric acid formed was determined by titration with a solution of potassium permanganate. The nitric oxide was considered to be pure if 50 cc. of it was completely absorbed by 25 cc. of the mixed acid.

Nitrous Oxide. The nitrous oxide was prepared by allowing a concentrated solution of pure sodium nitrite to drop slowly into a concentrated solution of hydroxylamine sulphate.

The nitrous oxide was determined after the removal of the nitric oxide by measuring the decrease in volume that occurred when the gas mixture was burned with an excess of hydrogen over a red-hot platinum spiral in a slow combustion pipette. The solubility of nitrous oxide under the conditions of these experiments in the mixed acid used for the absorption of the nitric oxide, was found to be 2.06 cc., at 0°C, 760 mm. and dry.

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* Contribution from the Baker Laboratory of Chemistry at Cornell University.

[1] Bancroft: J. Phys. Chem., **28**, 475; Milligan: 544; Milligan and Gillette: 744 (1924); Coblens and Bernstein: **29**, 750 (1925); Nichols and Derbigny: **30**, 491; Joss: 1222 (1926).

[2] Ludwig and Hein: Ber., **2**, 671 (1869); Maumené: Compt. rend., **70**, 147 (1870); Dumreicher: Monatsheft, **1**, 724 (1880); Divers and Haga: J. Chem. Soc., **47**, 623 (1885); Gay: Ann. Chim. Phys., (6), **5**, 145 (1885); Chesneau: Compt. rend., **129**, 100 (1889); Kohlschütter: Ber., **37**, 3053 (1904).

[3] J. Phys. Chem., **28**, 544 (1924).

Nitrogen. The incombustible gas left after the burning of the nitrous oxide was considered to be nitrogen.

Hydroxylamine. The hydroxylamine was determined by reducing it to ammonia with an excess of a 20 percent solution of titanous chloride and distilling the ammonia as described below. Since there was no nitric acid present, it was not necessary to carry out the reduction in a solution buffered with sodium dihydrogen phosphate. The presence of stannous chloride has no effect upon the accuracy of this determination.

Ammonia. The ammonia was determined by distillation with steam, after the reducing salts had been oxidized by a solution of copper sulphate and an excess of a syrupy solution of sodium hydroxide had been added. The distillate was collected in an excess of standard 0.033 N. hydrochloric acid. The excess acid was titrated with standard 0.033 N. sodium hydroxide, using methyl red as indicator. In the middle of the distillation, a sufficient amount of a solution of sodium sulphide was added to precipitate all of the heavy metals as sulphides.

Stannous Chloride. The concentrated solutions of stannous chloride were saturated at room temperature with respect to $SnCl_2.2H_2O$. They were prepared by boiling hydrochloric acid with an excess of pure tin or by dissolving crystallized stannous chloride (Kahlbaum's *For Analysis*) in distilled water. When the latter method was used, it was necessary to add a small quantity of hydrochloric acid and boil with tin for a few minutes to reduce the small quantity of stannic tin which was present. No difference in behavior of the solutions prepared by the two methods could be detected. Dilute solutions of stannous chloride were made by adding the necessary amount of the saturated solution to freshly boiled and cooled distilled water. The strength of the dilute solutions of stannous chloride was determined by adding a known volume to an excess of a standard solution of iodine and titrating the excess iodine with a standard solution of sodium thiosulphate.

Titanous Chloride. The concentrated solution of titanous chloride used in these experiments was the Titanous Chloride, 20 percent, (Standardized) the LaMotte Chemical Products Company. The dilute solutions were made with freshly boiled and cooled distilled water. The titanous content of the dilute solutions was determined by adding a measured volume to an excess of a solution of ferric alum and then titrating the ferrous iron with a standard solution of potassium permanganate in the presence of manganous sulphate and phosphoric acid.

It was originally planned to study the reduction of nitric oxide in a manner similar to that used by one of us[1] in the work on nitrous oxide. In this method, however, the gas is always mixed with a large amount of carbon dioxide and the solution of the reducing agent is saturated with carbon dioxide. Thus the exact partial pressure of the oxide of nitrogen is known only at the beginning of an experiment and decreases to some unknown smaller value as the reduction removes the reacting gas, which introduces an uncontrollable variable. Also the previous work on the reduction of both nitric oxide and nitrous oxide indicated that the reduction products were solids, ammonium or hydroxylamine compounds, or a relatively insoluble gas, nitrogen, and it was probable that these same products would be obtained in the present experiments so a simpler apparatus, as shown in Fig. 1, was used.

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[1] Nichols and Derbigny: J. Phys. Chem., 30, 491 (1926).

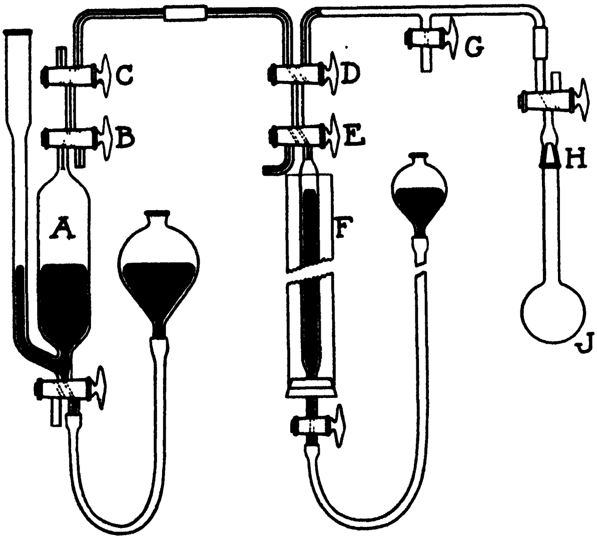

FIG. 1

Apparatus. The apparatus was made up of three parts, the nitrometer A, the burette F and the reaction bulb J. The nitrometer was modeled after the one described by Dennis[1] but differed from this in that the upper stopcock B was permanently sealed to the bulb and a second two-way stopcock C was sealed to B. One outlet of C was open to the air, the other was suitably bent for attaching to a burette by means of rubber tubing. For convenience of manipulation, two two-way stopcocks, D and E, were sealed to the top of the burette, This allowed either the nitrometer or the reaction bulb to communicate with either the burette or the air. The burette was of 50 cc. capacity and was calibrated with mercury from the bottom of the upper stopcock D. A water jacket, in which the water was constantly agitated by a slow stream of air, was used to keep the temperature uniform. The reaction bulb J was spherical in shape and had a capacity of 60 cc. It was connected to the burette by a ground glass slip-joint, H, and by a piece of enameled rubber tubing cemented in place. The tubing was sufficiently flexible to permit the shaking of the reaction bulb. A connection, G, for a water suction pump was inserted between the bulb and the burette.

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[1] Dennis and Nichols: "Gas Analysis", 428 (1929).

The apparatus was tested by filling the reaction bulb with distilled water, evacuating and then shaking the water with a measured volume of nitric oxide for one-half hour. The gas was then pumped off, measured and analyzed. There was no decrease in volume of gas and the gas was found to be completely soluble in the mixed acid.

Procedure. A measuring flask, calibrated to hold four times the volume delivered by a 25 cc. pipette, was filled with a solution of the reducing agent. Two 25 cc. portions, measured with the pipette used to calibrate the flask, were put into the reaction bulb J. A third 25 cc. portion was used for a blank hydroxylamine determination. The volume remaining in the flask was washed out with distilled water and was used for a blank ammonia determination.

The reaction bulb, containing the reducing agent, was attached to the apparatus by the slip-joint H. The apparatus was then evacuated, most of the air being removed through stopcock G with a water suction pump, the rest by using the burette F as a pump. During the evacuation, the bulb was shaken vigorously and the pumping was continued until all of the uncondensible gas was removed. This condition was indicated by a sharp click as the mercury struck the lower side of stopcock D, when the pressure in the burette was brought to atmospheric.

The nitrometer A, containing about 125 cc. of nitric oxide was connected as shown. The air was driven from the connecting system through the small jet on stopcock B by raising the level-bulb attached to the burette. Slightly less than 50 cc. of nitric oxide was run into the burette, stopcock C was closed and the gas was allowed to stand a few minutes to become saturated with water vapor at the temperature of the water jacket The volume at atmospheric pressure, the temperature of the water jacket and the barometric pressure were recorded. Stopcock D was reversed and the gas was run into the bulb J until the pressure in the system was atmospheric. Atmospheric pressure was maintained by keeping the mercury in the level-bulb at the same height as the mercury in the burette. The bulb was shaken throughout the time of reaction and if all of the gas was absorbed before the end of the reaction, additional portions of the gas were measured and added in the same way. Before the end of the period of the reaction, the nitrometer, without being detached, was cleaned of acid and mercurous sulphate and washed with distilled water. It was then filled with mercury to stopcock C.

At the end of the reaction, the gas remaining in the burette was forced into the nitrometer and the gas in the bulb J was pumped out and also stored in the nitrometer. When the bulb was completely evacuated, all the gas in the connecting system was driven into the nitrometer and stopcock B was turned through 180° to preserve the gas for analysis. Bulb J was detached and, using the same pipette as before, 25 cc. of the solution was withdrawn for the determination of hydroxylamine. The remaining solution was washed out with distilled water and analyzed for ammonia.

25 cc. of mixed acid, for the absorption of nitric oxide, was put in bulb J and the system was again evacuated. The gas from the nitrometer was run into the burette, its volume and temperature determined, and then

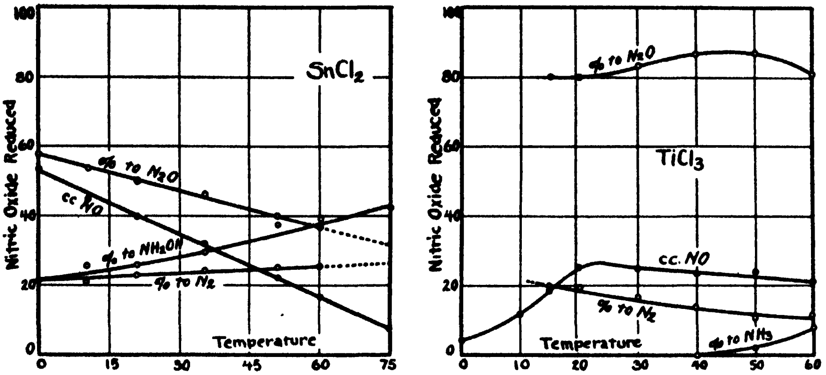

FIG. 2

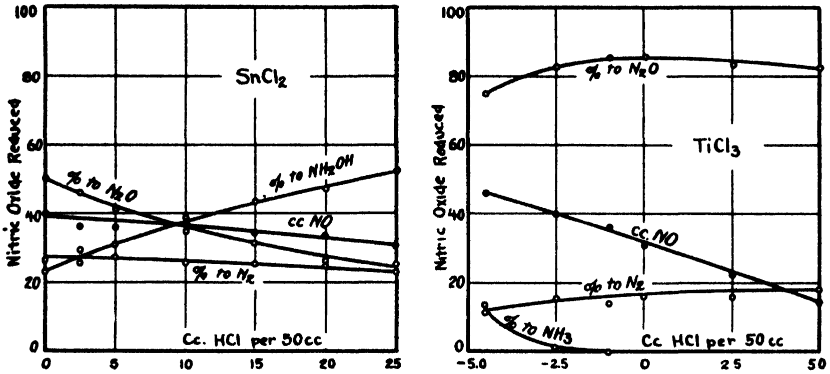

FIG. 3

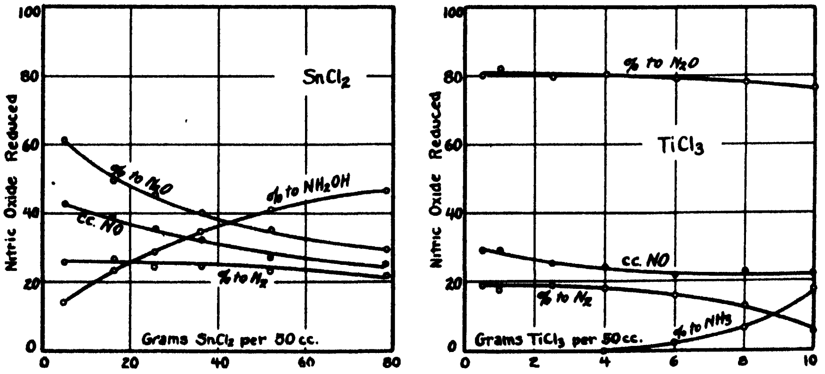

FIG. 4

transferred to the bulb. After five minutes contact, the gas was pumped out and stored in the nitrometer while a fresh 25 cc. portion of acid was put into the bulb. The absorption was repeated. After this second treatment, the volume and temperature of the residual gas were determined and the gas was again stored in the nitrometer. A second gas burette was attached to the free tube of stopcock E. The mercury from this burette was run through the connecting tube to stopcock B and a sample of the gas was withdrawn from the nitrometer. The burette, containing the sample, was detached and then connected to a slow combustion pipette for the determination of nitrous oxide.

Calculations. The volumes given in the tables are those at 0°C, 760 mm. and dry. The volume of nitric oxide not reduced is the volume of gas left after the treatment with the reducing solution minus the volume left after the treatment with mixed acid plus the volume of nitrous oxide dissolved in the acid (2.06 cc.). This volume subtracted from the volume of nitric oxide taken, i.e. the volume of nitric oxide as measured plus the volume of the tubing from the stopcock C to stopcock D, (0.4 cc.) gave the volume of nitric oxide reduced. The volume of nitrous oxide produced was the sum of the volume found by combustion and the volume dissolved in the mixed acid. In calculating the volume of nitric oxide equivalent to the weight of hydroxylamine or ammonia found, the weight of a liter of dry nitric oxide at 0°C, 760 mm. was taken as 1.340 g.[1]

Experimental. Using solutions of stannous chloride, the effects of the variation of the temperature, the acidity and the concentration of the rereducing agent were determined. The results of these experiments are given in Tables I, II and III and Figs. 2, 3 and 4. Similar experiments were performed using solutions of titanous chloride. In addition, the effect of different times of contact was determined. See Tables IV, V, VI and VII and Figs. 2, 3 and 4.

Table I

The Reduction of Nitric Oxide with Stannous Chloride.

Variation of the Temperature

Volume of Solution — 50 cc.
Concentration, $SnCl_2$ — 15.6 g./50 cc.
Time of Contact — 30 min.
Acidity — none

Temp., °C.	NO reduced cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_2OH
0	53.8	57.8	21.3	21.4
10	45.0	53.5	21.0	25.6
21	39.7	50.2	22.9	25.8
35	32.0	46.1	24.3	29.7
51	22.2	40.0	25.0	37.1
60	16.8	37.0	25.7	38.6
75	8.3	—	—	42.2

Note: the small volume of gas at 75° would not permit of an accurate analysis.

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[1] "International Critical Tables," 3, 3 (1928).

TABLE II

The Reduction of Nitric Oxide with Stannous Chloride
Variation of the Acidity

Temperature — 24.5° C.
Volume of Solution — 50 cc.
Concentration, $SnCl_2$ — 15.6.g./50 cc.
Time of Contact — 30 min.

cc. Conc. HCl per 50 cc.	NO reduced cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_2OH
0	39.4	50.1	26.8	23.5
2.5	35.2	46.4	25.6	29.1
5.0	35.3	41.5	27.8	30.5
10.0	36.8	38.7	25.5	35.1
15.0	34.5	31.7	25.6	43.3
20.0	33.7	26.1	25.6	47.2
25.0	30.4	25.6	23.4	52.2

TABLE III

The Reduction of Nitric Oxide with Stannous Chloride
Variation of the Concentration of Stannous Chloride

Temperature — 22.5° C.
Volume of Solution — 50 cc.
Time of Contact — 30 min.
Acidity — none

Conc. $SnCl_2$ G./50 cc.	NO reduced cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_2OH
5.2	42.8	61.0	25.9	14.2
15.6	39.4	50.1	26.8	23.5
26.1	35.6	45.5	24.7	28.9
36.2	32.2	40.7	24.6	34.7
52.1	27.2	35.3	23.3	41.5
78.2	25.6	29.9	22.5	47.0
15.6[1]	47.8	51.7	26.2	21.1

Platinized platinum present.

TABLE IV

The Reduction of Nitric Oxide with Titanous Chloride
Variation of the Temperature

Volume of Solution — 50 cc.
Time of Contact — 30 min.
Concentration, $TiCl_3$ — 2.5 g./50 cc.
Acidity — No Acid added

Temp., °C.	NO reduced, cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_3
0	4.7	100		0
10	11.2	100		0
15	18.1	80.0	19.2	0
24	25.2	80.0	19.2	0
30	25.0	83.4	16.7	0
40	23.6	86.6	14.4	0
50	24.2	86.8	10.8	2.4
60	20.8	80.6	11.5	8.1

TABLE V

The Reduction of Nitric Oxide with Titanous Chloride
Variation of the Acidity

Temperature — 24.0° C.
Volume of Solution — 50 cc.
Time of Contact — 30 min.
Concentration, $TiCl_3$ — 2.5 g./50 cc.

cc. Conc. HCl per 50 cc.	NO reduced cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_3
−4.5	46.0	74.7	12.1	13.2
−2.5	40.1	82.7	15.3	1.3
−1.0	36.1	85.6	14.0	0
0	31.0	85.6	16.1	0
+2.5	22.4	83.5	16.0	0
5.0	14.9	82.5	18.2	0

Note: In the first three experiments a solution of sodium hydroxide, whose strength was equivalent to that of concentrated hydrochloric acid, was used.

TABLE VI

The Reduction of Nitric Oxide with Titanous Chloride
Variation of the Concentration of Titanous Chloride

Temperature — 24.0° C.
Volume of Solution — 50 cc.
Time of Contact — 30 min.
Acidity — Increases with concentration, $TiCl_3$

Conc. $TiCl_3$ g./50 cc.	NO reduced cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_3
0.5	29.4	80.2	19.3	0
1.0	29.3	82.5	17.4	0
2.5	25.2	80.0	19.2	0
4.0	24.6	80.8	18.4	0
6.0	22.1	79.5	16.0	2.6
8.0	23.2	78.8	13.4	6.8
10.0	22.5	76.5	6.1	17.6
10.0 + 2 cc. $FeCl_2$	48.4	61.2	21.7	16.1

TABLE VII

The Reduction of Nitric Oxide with Titanous Chloride
Variation of the Time of Contact

Temperature — 24.0° C.
Volume of Solution — 50 cc.
Concentration, $TiCl_3$ — 2 g./50 cc.
Acidity — No Acid added.

Time, Min.	NO reduced, cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_3
30	26.3	82.5	17.4	0
60	43.8	82.8	16.6	0
120	64.9	82.0	19.1	0

Miscellaneous Experiments

Attempts were also made to reduce nitrous oxide in the apparatus shown in Fig. 1. Various concentrations of stannous chloride and titanous chloride were used and the time of contact was varied from one-half hour to four hours. No appreciable reduction could be detected. A solution of titanous chloride to which sodium hydroxide had been added (Cf. Table V) had no effect. The presence of carbon dioxide produced no reduction. The addition of stannous chloride or ferrous chloride, possible catalysts, to solutions of titanous chloride induced no reduction. The apparatus previously used by Nichols and Derbigny was rebuilt and experiments were made in it to see if the glass surface catalyzed the reduction of nitrous oxide. However under the conditions existing at this time it was impossible to obtain any indication of a reduction of the nitrous oxide with either stannous chloride or titanous chloride.

The effect of the presence of platinized platinum on the reduction of nitric oxide by stannous chloride was also determined, Table III, Fig. 4. A similar experiment was tried with titanous chloride but it was found that at low pressures, hydrogen was continuously evolved at the platinum surface. To increase the solubility of nitric oxide in titanous chloride, 2 cc. of dilute solution of ferrous chloride was added. The effect of the ferrous salt is shown in Table VI.

The experiments of Coblens and Bernstein[1] on the reduction of silver hyponitrite by stannous chloride and titanous chloride were repeated. When titanous chloride was used, a gas, presumably nitrous oxide, was rapidly evolved but no qualitative test for ammonia could be obtained. With stannous chloride, less gas was given off and a faint ammonia test was obtained after treatment with a solution of titanous chloride. That the evolution of nitrous oxide in the first experiment was due to the large amount of hydrochloric acid used to stabilize the solution of titanous chloride, was shown by an experiment in which the acid was almost neutralized with sodium hydroxide before the addition of the silver hyponitrite. In this experiment, the evolution of gas was much more feeble and a faint test for ammonia was obtained. These tests were not sufficiently positive to say that silver hyponitrite can be readily reduced.

Discussion

Joss[2] has shown that the mixture of nitric and nitrous acids that results from the solution of nitrogen peroxide in water is undoubtedly due to the decomposition of nitrosic acid, the reaction being

$$2\ NO_2 + H_2O = H_2N_2O_5 = HNO_3 + HNO_2$$

An analogous reaction occurs when nitric oxide dissolves in water. An aqueous solution of nitric oxide has an electrical conductivity that is much higher than that of pure water, indicating that an acid solution is formed.[1] Salts of nitrohydroxylaminic acid, whose formula corresponds to two molecules of nitric oxide plus one molecule of water, have been prepared.[2] Sodium nitrohydroxylaminate decomposes into sodium nitrite, sodium hydroxide and nitrous oxide when boiled with water.[3] Aqueous solutions of nitric oxide have been observed to decompose, after standing several months, into nitrous acid and nitrous oxide.[4]

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[1] J. Phys. Chem., 29, 750 (1925).

[2] J. Phys. Chem., 30, 1222 (1926).

These reactions may be expressed

$$2\ NO + H_2O = H_2N_2O_3$$
$$H_2N_2O_3 = NOH + HNO_2$$
$$2\ NOH = H_2N_2O_2 = N_2O + H_2O$$

When reducing agents act upon aqueous solutions of nitric oxide they may act directly upon the nitrohydroxylaminic acid or upon the mixture of nitrous acid and nitroxyl. Since the latter view is not necessary to explain the reduction, it is simpler to consider that the nitrohydroxylaminic acid is reduced directly, although this may not be the case.

The rate at which nitric oxide is reduced will depend upon the rate of formation of the nitrohydroxylaminic acid and upon the velocity of the reducing reaction. Pressure, temperature, nature and concentration of reducing agent, and efficiency of mixing will affect the rate of solution as well as the total solubility of nitric oxide; and, consequently, the rate of formation and concentration of nitrohydroxylaminic acid. Temperature, acidity and concentration of the reducing agent will be factors in determining the speed of the reduction reaction. To eliminate pressure and mixing variables, these factors were kept as constant as possible during the previously described experiments.

When using solutions of stannous chloride of constant concentration as reducing agents, the quantity of nitric oxide reduced in one-half hour decreases almost linearly with rising temperature (Table I, Fig. 2), while with titanous chloride, a pronounced maximum is produced at about 25°C (Table IV, Fig. 2). Since an increase in temperature should accelerate the chemical reduction and thereby tend to increase the amount of nitric oxide reduced in a unit time, these results show that, at all temperatures above 0°C, the speed of the reaction between stannous chloride and nitrohydroxylaminic acid is greater than the rate of formation of the acid. But with titanous chloride, at temperatures below 25° C, the speed of the reduction is slower than that of the formation of nitrohydroxylaminic acid, while at higher temperatures, the decreasing solubility of nitric oxide causes the opposite to be true.

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[1] Joss: Op. cit., 1270, 1271.

[2] Thum: Monatsheft, **14**, 294, (1893); Angeli and co-workers: Gazz., **26II**, 17 (1896); **27II**, 357 (1897);**30I**, 593 (1900); 31II, 15 (1901); **33II**, 245 (1903).

[3] Angeli and Angelico: Gazz., **30I**, 593 (1900).

[4] Russell and Lapraik: J. Chem. Soc., **32**, 35 (1877); Cooke: Chem. News, **58**, 155 (1888); Zimmermann: Monatsheft, **26**, 277 (1893).

The quantity of nitric oxide reduced in one-half hour decreases when the acidity of the solutions of the reducing agents is increased. This diminution in rate of reduction is slight in the case of stannous chloride (Table II, Fig. 3) but, with titanous chloride, it is very marked (Table V, Fig. 3). It is known that the reducing power of stannous chloride becomes greater as the concentration of acid is increased, while that of titanous chloride becomes less.[1] The effect of the concentration of acid upon the rate of reduction may be attributed to two causes; first, the different reducing power of the reagent and, second, the lower concentration of nitrohydroxylaminic acid in the more acid solutions. When these two factors are opposing one another, as in the case of stannous chloride, they produce little effect, but when they are working in the same direction, as they do with titanous chloride, the resulting change is great.

With both stannous chloride and titanous chloride solutions, increasing the concentration of reducing agent decreases the amount of nitric oxide reduced in unit time (Tables III and VI, Fig. 4). It has already been shown that the reducing reaction is the more rapid one at room temperature and above. This means that anything tending to increase the rate of this reaction will have no effect unless it influences something other than the speed of the reducing reaction. The addition of reducing agent decreases the rate of solution of the nitric oxide, its total solubility or both and thus causes a decrease in the rate of reduction.

That the rate of solution of nitric oxide is the factor determining the rate of reduction is shown by the experiments in which platinized platinum was added to a solution of stannous chloride, and ferrous chloride to titanous chloride. The volume of nitric oxide reduced in one-half hour was increased in both cases (Tables III and VI).

The reducing power of both stannous chloride and titanous chloride is sufficiently great to reduce the oxides of nitrogen to ammonia.[2] The presence of compounds intermediate between the oxide and ammonia may be accounted for in two ways; first, by secondary reaction between the reduced product and the original, more oxidized compound and, second, by decomposition of intermediate products before further reduction takes place. The first assumption does not seem to be tenable in the case of these experiments as it is very doubtful that oxidation of the reduced products will occur in the presence of large quantities of reducing agent, especially when the concentration of the oxidizing agent is small. It is more probable that the second is the true explanation.

The intermediate products in the reduction of nitrohydroxylaminic acid are hyponitrous acid $H_2N_2O_2$, the hypothetical compound $H_4N_2O_2$ and hydroxylamine. The first two decompose giving nitrous oxide and nitrogen, respectively. The difficulty of reducing nitrogen is well known and it has been found practically impossible to reduce nitrous oxide under the conditions of the present experiments. Thus it is seen that if these two gases are once evolved, there can be no further action of the reducing agent upon them and they will appear in the final product. The proportion of nitrous oxide and nitrogen in the product, will depend upon the relation of the speed of the decomposition reactions to the speed of the reduction reactions but, unless the rates of decomposition are zero, both gases will be present.

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[1] Nichols and Derbigny: J. Phys. Chem., 30, 504 (1926).

[2] Joss: J. Phys. Chem., 30, 1260 (1926).

Increasing the temperature will increase the velocity of both the decomposition and the reduction reactions, and, since these oppose each other, the net effect will be due to that reaction whose rate changes more rapidly. With stannous chloride solutions, the proportion of nitrous oxide decreases with rising temperature (Table I, Fig. 2). This shows that the rate of reduction increases more rapidly than the rate of decomposition. With titanous chloride solution the opposite is true, i.e., the rate of decomposition of hyponitrous acid increases more rapidly than the rate of reduction (Table IV, Fig. 2).

At higher temperatures stannous chloride solutions produce a greater proportion of nitrogen than they do at lower temperatures (Table I, Fig. 2). In this case the rate of decomposition of $H_4N_2O_2$ increases faster than the rate of reduction. The reverse takes place with titanous chloride solutions, i.e., the rate of reduction increasing more rapidly than the rate of decomposition (Table IV, Fig. 2).

The other experiments show the same effect. An increase in the concentration of acid increases the reducing power of solutions of stannous chloride and decreases that of titanous chloride. Tables II and V and Fig. 3 show that in the first case the proportion of nitrous oxide and nitrogen diminishes with increasing acidity, while in the other it increases. Greater concentrations of reducing agent will accelerate the rate of reduction and thus decrease the proportion of nitrous oxide and nitrogen in the product as shown by Tables III and VI, Fig. 4.

Since any hydroxylamine that is formed remains in solution as such it can be reduced further if the reducing agent is sufficiently powerful. If the reduction of hydroxylamine to ammonia is a rapid reaction, no hydroxylamine will appear in the final product. This is the case when titanous chloride is the reducing agent. But, when stannous chloride solutions are used, the rate of reduction of hydroxylamine to ammonia is very low and, unless the solutions are allowed to stand for several hours, no ammonia can be found.

From the above discussion, it is seen that the composition of the product obtained by the reduction of nitric oxide with reducing agents strong enough to carry the reduction to ammonia depends almost entirely upon the relative rates of several reactions. Any catalytic effect of the reagent or of its oxidation product upon one or more stages of the reduction is probably the main factor in determining the chief components of the final product of the reduction.

Summary

1. Nitric oxide dissolves in water to form nitrohydroxylaminic acid, $H_2N_2O_3$, or a compound of the same constitution.

2. At temperatures above 0°C the rate of reduction of nitric oxide by stannous chloride depends wholly upon the rate of formation of nitrohydroxylaminic acid.

3. At temperatures below 25°C the rate of reduction of nitric oxide by titanous chloride depends upon the speed of the reduction reaction, at temperatures above 25°, the formation of nitrohydroxylaminic acid is the limiting factor.

4. The reduction of nitrohydroxylaminic acid proceeds through various intermediate stages which may be represented

$$H_2N_2O_3 \rightarrow H_2N_2O_2 \rightarrow H_4N_2O_2 \rightarrow H_2NOH \rightarrow NH_3$$

5. Nitrous oxide and nitrogen are the result of the decomposition of hyponitrous acid and $H_4N_2O_2$, respectively, and, since these decompositions have sensible velocities, they will always be present in the products. The relative proportion of these gases in the final product depends upon the relation of the speed of the decomposition reaction to the speed of the reducing reaction.

6. Hydroxylamine is the apparent end-product when stannous chloride is the reducing agent because of the extreme slowness of the rate of its reduction to ammonia by this reagent.

7. Any catalytic effect by the reagent or oxidation product of the reagent upon one or more stages of the reduction will have a marked influence upon the composition of the product obtained by the reduction of nitric oxide.

REAGENT CONCENTRATION IN THE WALDEN INVERSION*

BY WILDER D. BANCROFT AND HERBERT L. DAVIS

In the thirty-five years that have passed since Walden discovered what Fischer later called, "the most surprising observation in the field of optically active substances since the fundamental investigations of Pasteur" and to which he gave the name "the Walden Inversion," countless perplexed chemists have made repeated attacks on the problem presented, but the actual increase in our knowledge of the essential conditions which determine whether or not a given reaction will be accompanied by an inversion is very slight. Walden[1] himself, concluded a recent discussion of the problem with these words:

"Finally, chemical theory and scientific speculation in general were stimulated to a remarkable degree by this discovery. An explanation, a theoretical basis, was necessary for this new group of facts which ran contrary to all current theoretical ideas.

"Actually, the reality has surpassed all expectations. Up to the present time no less than twenty-five theories have been advanced to explain this phenomenon. The discoverer of this inversion has had the unusual honor of seeing the most influential men gathered around his 'brain child.' They have bestowed gifts upon this child, and many of them have proposed chemical or physical theories to explain the nature of this phenomenon. Although in the meantime this child has grown up, and has reached the age of thirty years, chemists who are studying the configuration of molecules still regard it as an *enfant terrible*. Although many suggestions have been advanced to explain the phenomena grouped under the 'Walden Inversion,' a completely satisfactory solution has not yet been attained nor has it been found possible to predict the course of an inversion."

The present paper will show that there are certain conditions which have a determining effect on the course of such reactions and that in the conversion of halosuccinic acids to malic acid a very important condition is the acidity or the concentration of the reagent.

In the years preceding 1896 the foundations of organic chemistry had been laid on the fundamental assumption that reactions of replacement go directly, the replacing group occupying the same relative position in the molecule as had been occupied by the displaced radical. In 1896 Walden published the first results which showed that this is by no means always the case and that sometimes displacing groups take other positions in the molecule than that of the displaced group. Proof of this had to rest on the optical rotatory power of the molecules concerned and can today be demonstrated only for those

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* This work is part of the programme now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Walden: "Salts, Acids, and Bases: Electrolytes: Stereochemistry," 384 (1929).

molecules which rotate the plane of polarized light. None of the other common properties lend themselves to distinguishing between optical enantiomorphs although the same type of reactions must occur also in optically inactive molecules. It makes no difference whether the entering chlorine atom definitely takes the place of the hydrogen atom it displaced in forming methyl chloride, for the remaining hydrogens are all alike and the product molecules have identical properties. But if the three attached groups are all different from each other and from the entering group the result will be the formation of an optically active carbon atom and if in one reaction the entering group replaces a group directly while in another reaction it enters at a different position, the result will in both cases be optically active carbon atoms and they will be mirror images of each other, turning the plane of polarized light in opposite directions, and hence called optical antipodes. This was somewhat equivalent to adding a Bohr-like dynamic concept to the previously accepted and very useful static tetrahedron picture of the carbon atom, and produced similar disquietude.

Some of the history of the problem will aid in its comprehension. The optical rotatory power of certain substances was discovered by Malus in 1808 and studied extensively by Biot. About 1850 Pasteur carried out his epoch-making investigations which related rotation and crystal form and established that the oppositely rotatory types of certain salts of tartaric acid form crystals which are mirror images of each other. In 1874 van't Hoff and Le Bel, studying the work of Pasteur, hit independently upon the idea of the asymmetric carbon which still remains the best theoretical basis for the study of optical activity. No one yet has been able to explain why a carbon atom which is attached to four different groups or atoms can rotate the plane of polarized light, but it is a fact of nature.

The attempt to measure the effect and to predict it was made by Guye in 1890. He assumed that the relative masses of the attached atoms or groups is a measure of the rotatory power of the molecule and was able to apply his criterion to some optically active compounds. It was while Walden was attempting to test the validity of van't Hoff's theory and that of Guye that Walden discovered the Walden Inversion.

The first idea of Walden was to discover if a mere difference in the four groups attached to the carbon atom was sufficient to impart optical activity. Working at low temperatures he was able to convert l-malic acid, by the use of phosphorus pentachloride, to chlorosuccinic acid which proved to be strongly dextrorotatory,[1] this being the first preparation of this acid in an active form.

Two years later he returned to the same problem, "to determine by repetition and variation of the previously reported negative reactions, whether inactivation on displacement of hydroxyl groups by chlorine or bromine is a consequence of the specific properties of these halogens or whether the conditions of the previous researches made racemization inevitable and that therefore the observed exceptions are only apparent." Walden[1] used PCl_5 and PBr_5 instead of HCl and HBr and reported the preparation and properties of several derivatives of chlorosuccinic and other active acids, treating not only malic but also tartaric and lactic acids to form the halogen derivatives and retaining optical activity in all. He therefore confirmed the conclusion that a difference in the four groups bound to the carbon atom is the only necessary condition for optical activity and that the specific nature of these groups determines only the magnitude and direction of the rotation. Later in the same year he reported the formation of dextro and levorotatory bromosuccinic[2] acids from the same levorotatory asparagine.

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[1] Walden: Ber., **26**, 210 (1893).

The next paper[3] in the series is really the most important of all for in it was reported the first optical cycle. "We have then the following cyclical process: starting with l-malic acid we prepared (by PCl_5) a chlorosuccinic acid which is dextrorotatory; in this dextro-acid we replace chlorine by hydroxyl and obtain a malic acid which is just as dextrorotatory as and which represents the optical antipode to our starting-out material. If we treat this dextro-malic acid again with PCl_5 there results a levorotatory chlorosuccinic acid which is the optical antipode to the first mentioned chlorosuccinic acid. On displacing the halogen by hydroxyl again this acid is converted to levorotatory malic acid the material first used." Thus Walden changed an optically active substance into its optical antipode without racemizing and resolving.

This work was continued with the conversion of l-bromo- or l-chlorosuccinic acids into a dextrorotatory amino succinic acid which in turn produced d-malic acid.[4] Ammonia gave a change in the direction of rotation but silver oxide in the same reaction gave an opposite result. Then as a very useful aid in the following of these reactions which involve malic acid the use of uranyl nitrate was described.[5] Pure malic acid in aqueous solution gives a specific rotation, $(a)_D = -0.77°$, but when the aqueous or alcoholic solution of malic acid contained for every mol of malic acid 4 mols of KOH and one to four mols of uranyl nitrate, the rotation became $(a)_D = -475°$. Similar changes were wrought on some other active substances but d-chlorosuccinic acid remained practically unchanged and l-bromosuccinic acid decreased its rotation slightly on addition of uranyl nitrate. This type of activation seems restricted to alpha hydroxy acids and has been shown to be associated with a tautomeric equilibrium in such compounds.[6] Walden practically always used the solutions as above or with ammonia in place of KOH, and Holmberg has followed him in this.

The next paper[7] in the series reported the effect of potassium hydroxide on the halosuccinic acids. It was shown that KOH or ammonia on a given halogen-substituted succinic acid gave malic acid of the opposite rotatory power while silver oxide in the same reaction produced a malic acid of the same direction of rotation as the original chlorosuccinic acid.

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[1] Walden: Ber., **28**, 1287 (1895).
[2] Walden: Ber., **28**, 2766 (1895).
[3] Walden: Ber., **29**, 133 (1896).
[4] Walden and Lutz: Ber., **30**, 2795 (1897).
[5] Walden: Ber., **30**, 2889 (1897).
[6] Bancroft and Davis: J. Phys. Chem., **34**, 897 (1930).
[7] Walden: Ber., **30**, 3146 (1897).

Then Walden[1] prepared a summary of the work and included new experiments designed to show the effect of various hydroxides on the hydrolysis of the halosuccinic acids, and attempting to discover which type of reaction represented normal and which abnormal replacement. These papers include the data for the reactions in the presence of seventeen oxides and hydroxides. Five of the systems were homogeneous while the rest contained the suspended, difficultly soluble, base. The whole comparison has several inconsistencies in it but has long served to baffle chemists. All of the experiments were started with levorotatory chloro- or bromosuccinic acid. The hydroxides can be arranged in a series ranging from silver oxide which gave practically only l-malic acid to ammonium hydroxide which gave equally pure d-malic acid as indicated by the specific rotation in presence of uranyl nitrate. In order these compounds are: Ag_2O, H_2O, TlOH, HgO, Hg_2O, PdO all gave levorotatory mixtures of decreasing rotatory power, Tl_2O_3 gave an inactive malic acid, and the following gave dextrorotatory mixtures of increasing rotatory power: LiOH, $Sn(OH)_2$, NaOH, $Pb(OH)_2$, $Ba(OH)_2$, $Cd(OH)_2$, CuO, KOH, RbOH, NH_4OH. It should be emphasized that these results are not truly comparable; for the conditions, concentrations and methods of handling were scarcely alike for any two substances. These considerations are mentioned in no criticism of this pioneer work of Walden who admits that he had difficulty getting any reproducible results at all, but possibly to explain why this table does not appear to fall in line with any other properties of the substances concerned.

We are therefore in a position to formulate simply the essential problem of the Walden inversion in terms of the compounds studied by Walden who showed these reactions to take place:

$$\begin{tikzcd}
 & & \text{l-malic acid} \\
\text{l-malic acid} \arrow[r, "PCl_5"] & \text{d-chlorosuccinic acid} \arrow[ur, "KOH"] \arrow[dr, "Ag_2O"'] & \\
 & & \text{d-malic acid.}
\end{tikzcd}$$

Evidently in passing from l-malic to d-malic acid we have changed the relative position of the hydroxyl group and thus changed the configuration of the optically active molecule. In which of these two sets of reactions did inversion take place? If PCl_5 substituted the chlorine atom in a position other than that originally occupied by the hydroxyl group then this is inversion and the action of the silver oxide is normal, while that of the potassium hydroxide is abnormal or accompanied by inversion. But if the PCl_5 reaction is normal then that of the potassium hydroxide is also, while the silver oxide is abnormal. The crux of the Walden Inversion problem is the question: do malic and chlorosuccinic acids having the same configuration also possess the same sign of rotation? In thirty-five years we have not found the answer to that question that could be accepted, as witness the statement of Holmberg[1] recently. After a critical survey of recent work on d- and l-isomers of lactic, malic, succinic acids, etc., and more than thirty years of work on them himself, he concludes that there is no general method available for ascertaining the configuration of mirror image isomers. Those offered are objectively unsatisfactory and allow subjective evaluation of evidence leading to conflicting conclusions. But real progress can be made in this field only by postulating one thing or the other and discovering where the postulate will lead. For reasons which will be elaborated in a forthcoming paper it appears to us reasonable to assume that malic acid and chlorosuccinic acid having the same configuration will also show the same sign of rotation. This is not a general rule and the criterion must be worked out for each set of compounds. It so happens that the bromosuccinic and iodosuccinic acids of the same configuration as malic acid will have the same sign of rotation. This will be reverted to, but first its seems advisable to survey some of the more recent work on the Walden Inversion, especially that of Holmberg.

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[1] Walden: Ber., **32**, 1833, 1855 (1899).

In 1912 Holmberg[2] started what has probably been the soundest work done on the Walden Inversion. He attacked the problem by the kinetic methods of physical chemistry and one of his early experiments made a study of the hydrolysis of chlorosuccinic acid by neutralizing the acid and following its rotation and the amount of alkali needed to keep it alkaline to phenolphthalein, and the amount of chlorine ions split off (titration with silver nitrate). The rotation of his solution started at $-4.17°$ and at the end of 102 hours was $-1.08°$, having passed through a minimum at $-0.42°$. The base used rose very slowly, while the silver titration rose quite rapidly, in a manner rather similar to the rotation. The curves so obtained were interpreted as follows: "The l-bromo anion decomposes quickly into the bromine and lactone acid anions, the latter being dextrorotatory. In neutral solutions the lactone is hydrolyzed only slowly, but as malic acid is formed, the H^+ catalyzes the process but retards the lactone formation, and when enough of the d-rotatory lactone has been converted into the feebly rotatory malic acid, the l-rotation begins to increase owing to the presence of undecomposed l-bromosuccinic acid." The Walden Inversion may therefore be represented thus:

l-bromo acid → d-malic acid lactone → d-malic acid.

The confirmation of this conclusion has been the purpose and the result of much of Holmberg's subsequent work in this field and has brought to light some very interesting data.

The following year Holmberg[3] published more complete accounts of similar experiments extending to l-chloro-, l-bromo-, and l-iodo-succinic acids. He showed that if l-bromosuccinic acid be neutralized and set aside, the solutions becoming acid by reason of the hydrolysis process, the product was mainly (74%) l-malic acid. Then by adding sodium hydroxide so that the solution was alkaline most of the time he showed that "the malic acid lactone formed from the sodium salt of l-bromosuccinic acid forms principally d-malic acid on alkaline hydrolysis". This is represented by:

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[1] Holmberg: Svensk. Kem. Tid., **41**, 60 (1929); Chem. Abs., **23**, 3441 (1929).

[2] Holmberg: Ber., **45**, 1713 (1912).

[3] Holmberg: J. prakt. Chem., **87**, 456 (1913).

l-bromosuccinic acid as sodium salt
↓
dextrorotatory, bromine-free, intermediate product
In alkaline solution | | In acid solution
↓ ↓
d-malic acid l-malic acid

Further experiments demonstrated certain properties of this lactone; it is stable in neutral solution; but in acids and yet more rapidly in alkaline solution it is converted into malic acid; it is chemically active; its conversions are accompanied by little racemization. Holmberg[1] believed that no change in configuration takes place and says: "Since from the change of rotation of a neutral solution of sodium bromosuccinate it must be concluded that the resulting malic acid lactone is dextrorotatory, at least in aqueous solution, this acid will be designated as the d-acid, and therefore the l-bromosuccinic acid and the d-malic acid lactone must be of the same configuration." Actually there is nothing to show that this is true or that the lactone is really formed by inversion in the first step.

In 1927 Holmberg[2] returned to this problem in a series of papers. Some experiments on the alkaline decomposition of chlorosuccinic acid showed that the velocity constant of the bimolecular reaction for the hydrolysis to malic acid is dependent on the kind and concentration of the metallic ions present. The second paper is entitled, "The Hydrolysis of Monohalogen Succinic Acids," and represents one of the best pieces of work done on the Walden Inversion. In his review of his earlier work he says: "Since the influence of ammonia on the dextro-malic acid lactone causes the formation of dextro-β-amido malic acid, we recognize the d(−) configuration for that acid, and since the (alkaline) saponification of this form (to be indicated as d(+) malic acid lactone), leads to d(+) malic acid we conclude that the influence of hydroxyl ions on the malic acid lactone is without inversion. For similar reasons we may conclude that the addition of other ions will likewise proceed without inversion, and since finally, the halogen- and sulphur-substituted succinic acids from d(+) malic acid are levorotatory, one must indicate these acids as the d(−) form." Again this appears to be merely an assumption and the opposite assumption would explain the facts and be about as well justified.

The experiments of this paper, however, are quite interesting. A glance at the list of reagents used by Walden would suggest the possibility that the character of the product resulting from the hydrolysis of chlorosuccinic acid might be influenced by the acidity of the medium. In general those oxides which are the weakest as bases gave a preponderance of the l-malic acid, while the strong bases gave d-malic acid. For such a substance as sodium hydroxide which should give a large quantity of d-malic the lower yield is to be attributed to the too vigorous action of the alkali leading to more racemization and to the formation of fumaric acid which had prevented so much of the earlier work from bearing fruit. Also most of Walden's experiments involved variable amounts of heating and these compounds are easily racemized by heating, especially the halosuccinic acids. Holmberg also had this idea about the acidity of the medium and a group of experiments show that starting with levorotatory chlorosuccinic acid, hydrolysis resulted in an excess of the d-malic acid in alkaline solutions and in an excess of l-malic acid in acid solutions. The relative proportions of these forms is roughly proportional to the acidity or basicity of the solutions. Indicators were not used but additions of acid or of base kept the solutions approximately in the required condition.

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[1] Holmberg: J. prakt. Chem., **88**, 553 (1913).

[2] Holmberg: Ber., **60**, 2194, 2198 (1927).

We have confirmed these findings of Holmberg in regard to the course of this hydrolysis. A first attempt to prepare chlorosuccinic acid by the use of malic acid and phosphorus pentachloride[1] met with limited success, the same difficulties being encountered as were met by Walden. The yield is low, much of the product being fumaric acid. However, some d-chlorosuccinic was thus prepared and hydrolyzed. The principal amount of the halosuccinic acids used was prepared by the methods of Holmberg (1927).

Actually Walden had used some asparagine and aspartic acid as sources of chlorosuccinic acid but Holmberg perfected the method and made quantities. The Holmberg method consists in treating aspartic acid in the presence of NaCl and HCl with sodium nitrite. The reaction proceeds nicely, requires no heating at any time and apparently always works. Holmberg reported 14-15 grams of chlorosuccinic acid from 15 grams of aspartic acid. Three separate preparations have borne this out both as to quantity and quality of yield. The acid prepared has properties that check with those reported by Holmberg.

Then came the problem of hydrolyzing the acid under conditions of approximately constant pH and for this it was decided to use suitable buffer solutions which were checked by means of the hydrogen electrode. Since the reaction used up hydroxyl ions, fresh alkali must be added to keep the pH up to the required value. The chief difficulty in the experiment was to get reliable readings from the platinum-hydrogen electrode in the alkaline solutions, so much so that good control proved impossible under the conditions. We shall therefore present only the qualitative results. Possibly the repetition of such an experiment with suitable indicators will prove of interest later.

As buffer solutions, the glycocoll-sodium hydroxide mixtures were found to be the only common ones covering the range desired, namely from pH 9 to pH 13. Buffer solutions were made up for pH 9, 10, 12, and 13, the solution for pH 11 being omitted because the titration curve at that point is steeper and the solution would be more sensitive.

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[1] Walden: Ber., **29**, 133 (1996).

The plan for the runs was to take four grams of the chlorosuccinic acid neutralized by sodium hydroxide and diluted to 50 cc. To this 50 cc of the appropriate buffer solution was added and the pH determined, more alkali being added as necessary, the attempt being made to keep each solution within 0.3 units of the indicated pH value.

The progress of the inversion can be followed by the change in the polarimetric readings since it has been shown that the presence of the glycocoll and excess base has no appreciable effect on the rotation of the two acids concerned. These solutions will thus contain sodium chlorosuccinate and glycocoll and will develop sodium malate. Solutions A, B, C, and D contain chlorosuccinic acid or its sodium salt while solutions M, N, O, and P contain malic acid or its sodium salt. In solution A one gram of chlorosuccinic acid was dissolved in 25 cc of solution; in solution B one gram of this acid was neutralized by NaOH and diluted to 25 cc; in solution C one gram of the acid was neutralized and then diluted to 25 cc with buffer solution pH 9; while solution D contains one gram of the acid neutralized and diluted with buffer solution pH 13. Solutions M, N, O, and P were made up in the same way using 0.879 g of malic acid (equivalent to one gram of chlorosuccinic acid) in each 25 cc of solution. The observed rotations of these solutions were:

A	B	C	D
−0.84°	−1.11°	−1.11°	−1.09°
M	N	O	P
−0.05°	−0.35°	−0.35°	−0.35°

These results show that although the sodium salts of both of these acids are more strongly rotatory than the acids themselves, the presence of the glycocoll has no effect. The concentrations here taken represent the original and final concentrations of the ions if there were no dilution during the run. This dilution will affect the rotatory power of malic acid but will be comparable since the same amount of alkali will be required in each case.

In agreement with the findings of Holmberg the originally levorotatory chlorosuccinic acid in all these alkaline solutions was converted to dextrorotatory malic acid. The levorotation of the solutions decreased to zero and then became increasingly a positive rotation which in no case reached the value of +0.35°, the value for pure d-malic acid. The speed of this conversion is proportional to the hydroxyl ion concentration, the most alkaline solution becoming inactive optically at about 100 hours, while the solution in the pH 9 buffer required 200 hours at room temperature to reach zero optical activity. After that point the solutions became increasingly dextrorotatory appearing asymptotically to approach a limiting value which varied with the pH of the solution and indicated that the higher the pH of the solution the more did d-malic acid predominate in the product of hydrolysis. This experiment then completely confirms the findings of Holmberg and throws a new light on the

Walden Inversion. Apparently in those solutions in which the concentration of hydroxyl ions is high this ion is forced into the molecule of chlorosuccinic acid somewhat disruptively and in such a way that direct replacement is impossible and a Walden Inversion results. In acid solutions the hydrolysis results in the formation of l-malic acid as the final product.

As a method of preparing d-malic acid this procedure may be modified and gives very good results. The solution of chlorosuccinic acid is neutralized and heated on the water bath, fresh alkali being added in small portions just sufficient to keep the solution alkaline to phenolphthalein. In about one and one half hours the reaction is complete. The chloride may be precipitated by silver nitrate and the malic acid subsequently by precipitation as the lead salt and treatment of the suspension with hydrogen sulphide. Study of the d-malic acid thus prepared showed it to have the proper melting point and to possess exactly the same rotatory power as a sample of l-malic from Eastman.

There are other examples of the determining power of the hydroxyl ion concentration on the product of such an hydrolysis. Levene, who has probably done more work on this problem than any other American, reports[1] the hydrolysis of a dextrorotatory propylene oxide. He finds that a comparatively high hydrogen ion concentration of the hydrolysis medium leads to a dextrorotatory glycol while a high hydroxyl ion concentration leads to a levorotatory glycol.

Hydrolysis in Presence of Silver Oxide

In addition to acidity Holmberg showed also that the amount of reagent present controlled the product resulting from hydrolysis of the halosuccinic acids. In the early work Walden had been much mystified that the action of silver oxide and of potassium hydroxide on a chlorosuccinic acid produced malic acids which were alike chemically but which were opposite stereochemically. In other words the formation of one acid involved an inversion and some of the theories proposed to account for the Walden Inversion have started from this point, calling attention to the greater tendency for the silver to abstract the chlorine more forcibly (and with the possibility of inversion) from the chlorosuccinic acid. In the treatment of chlorosuccinic acid it must be borne in mind that three molecules of such a base as sodium hydroxide will be required per molecule of free acid used, two of these forming the salt and the third furnishing the hydroxyl group for the molecule.

In 1913 Holmberg said: "Of my experiments I will now describe a few decompositions with silver oxide because they show that in the case of l-bromosuccinic acid there exists no essential difference in regard to the activity of the malic acid formed between this base and sodium hydroxide." The experiment indicated that starting with just enough silver oxide to form the silver bromosuccinate and letting the solution stand for thirty days (solution becoming acid), the malic acid obtained was 64% l-malic acid: while if 60% more silver oxide were used (a solution tending to have a more alkaline reaction) the product contained 65% d-malic acid.

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[1] Levene and Walti: J. Biol. Chem., 73, 263 (1927).

In the 1927 papers Holmberg returned to this feature of the problem and attempted to explain some of Walden's results with the heavy metals, where the solution could not have been strongly alkaline but in which dextrorotatory malic acid was obtained. It becomes necessary then to assume some catalytic activity for the metal ion complexes, especially since copper and lead are notorious for the formation of these complexes with oxygen acids. The experiments show that cupric ions favor the formation of d-malic acid so effectively that this influence is evident even in solutions which are undoubtedly acid. Beryllium and aluminum ions act similarly while magnesium and calcium have little effect. Identical solutions were prepared of the sodium salt of the malic acid lactone; left standing alone it produced l-malic acid (solution becoming acid), with addition of sodium hydroxide or of copper sulphate there formed some dextrorotatory malic acid, and in presence of cadmium sulphate an inactive acid was the product. Of the effect of silver oxide Holmberg[1] says: "Since the researches of Walden the silver ion has played a special role in almost all investigations of steric behavior during the hydrolysis of halogen-substituted acids. In my earlier experiments with halosuccinic acids and silver oxide I have found no other influence of the silver ions than a vigorous acceleration of the lactone formation. From a somewhat different point of view I have adopted the views of Euler and of Biilmann concerning the cause of this acceleration. According to their view there is first formed an organic cation with positively charged carbon. The salt of a halogen-succinic acid gives an intermediate ion, $\overset{-}{O}\cdot CO\cdot \overset{+}{C}H\cdot CH_2\cdot CO\cdot \overset{-}{O}$, which might then momentarily change into the univalent anion of the lactone malic acid, while the corresponding cation in the case of a free halogen-succinic acid must show the composition, $HO\cdot CO\cdot \overset{+}{C}H\cdot CH_2\cdot COOH$. Of such an ion one must expect that it would change so slowly into lactone malic acid (and hydrogen ion) that it would also in appreciable amounts be converted directly to malic acid and hydrogen ion. This conversion should occur with inversion and in agreement with this the free levorotatory halogen-succinic acids in the presence of silver nitrate give strongly levorotatory malic acid, while their acid or neutral salts under the same conditions behave not markedly different than in the absence of silver ions." It may be borne in mind that Holmberg's earlier mechanism and still alternative picture for the hydrolysis of the ion is:

$$\overset{-}{O}\cdot CO\cdot CHCl\cdot CH_2CO\cdot \overset{-}{O} \longrightarrow \overset{-}{O}\cdot CO\cdot CH\cdot CH_2\cdot CO + Cl^-$$

anion of l-chlorosuccinic acid   anion of dextrorotatory malic acid lactone.

In order to confirm these findings of Holmberg and to extend them we have carried out some experiments hydrolyzing l-bromosuccinic acid in the presence of varying amounts of silver oxide. The acid was prepared from aspartic acid according to the method of Holmberg[1], 0.02 mol being taken for each experiment, and 2, 2.8, 3.2, and 3.6 equivalents of silver oxide respectively being added to the acid. The calculated amount of silver nitrate was treated with alkali, the precipitated oxide washed and added to the acid in 100 cc of suspension. Bottles containing these suspensions were fixed on a rotating cage in a thermostat bath at 40° for nine weeks.

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[1] Holmberg: Ber., 60, 2203 (1927).

At the end of that time the suspensions were treated with 1.4N HCl until no further precipitation of silver chloride took place. The final solutions from the hydrolysis could contain only undecomposed bromosuccinic acid, malic acid, the silver salts of these acids and excess silver oxide, consequently the acid addition left in solution only malic acid and possibly some undecomposed bromosuccinic acid. The silver chloride was filtered off and the filtrates concentrated under vacuum to 25 cc. Two-cc samples of these solutions were titrated with $Ba(OH)_2$ solution and the rotations of the malic acid determined in the presence of one mol of uranyl nitrate and four mols of ammonium hydroxide per mol of malic acid. Practically no undecomposed bromosuccinic acid was left, as was shown by the fact that the final solutions did not increase in acidity on standing several days (hydrolysis of remaining bromosuccinic acid would have been shown by increased acidity of the solution), and by the fact that further addition of silver nitrate later caused no formation of any silver bromide from bromide ion that might have been split off. In the presence of uranyl nitrate Walden had reported as high as −475° as the specific rotation of his malic acid, Holmberg gave and used −436° as his value; while the malic acid furnished by Eastman showed −418° as its specific rotation and this value has been used in the present run. The results of the silver oxide hydrolysis were:

Equivalents of silver oxide per mol of l-bromosuccinic acid	Specific rotation of malic acid product	Product
2	−148.8°	67.8% l-malic
2.8	+ 22.0	52.6% d-malic
3.0	+ 42.0	55.0% d-malic
3.2	+ 55.4	56.6% d-malic

These results show that the malic acid produced is dependent on the amount of silver oxide present and that the production of equivalent amounts of d- and l-malic acids would take place in the presence of about 2.7 equivalents of silver oxide per mol of bromo-succinic acid instead of the three equivalents called for by the stoichiometric proportions. The fact that such a change should follow is the more remarkable when one considers that these systems are all heterogeneous, silver chloride being formed from the suspended silver oxide. In the bath which was kept dark, the first sample gave a white precipitate at the end, while in the last vessel the solid was deep black with the excess silver oxide. In this case as in the alkali run the determining factor appears to be the chemical potential of the hydroxyl ion which is sustained at a higher level by the excess silver oxide in equilibrium with dissolved silver hydroxide. There may be a secondary influence due to the silver ions but certainly the dividing line between the production of d- or of l-malic acid does not come at pH 7, for all these solutions at the end were acid to litmus, even though three of them produced d-malic acid whose production is most favored in definitely alkaline solutions. It appears that that portion of the hydrolysis which takes place at the surface of the suspended silver oxide produced d-malic acid because of the higher pH there, while that hydrolysis which went on in the solution led to a l-malic acid and thus that a large factor in the experiments of Walden on the insoluble bases is the fineness of division and the character (activity) of the surface of the suspended oxide. It follows from this that we may not expect to obtain from such a suspension a much higher yield than 70 or 80% d-malic acid under the most favorable conditions in the presence of silver oxide, while a reaction in homogeneous solution of the proper alkalinity does lead to nearly complete conversion to d-malic acid.

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[1] Holmberg: Ber., **60**, 2194 (1927).

Walden has not been oblivious to this contention of Holmberg's to the effect that in the hydrolysis of the chlorosuccinic acids a determining factor was the hydrogen ion concentration of the hydrolysis medium, but in 1919 subjected[1] it to scrutiny and concluded that it had no validity for other series of compounds for which he found data in the literature. In view of what we now know of these phenomena this discarding of the work of Holmberg is not justifiable and appears to be based on two principal errors. In the first place there is no thought that in any hydrolysis of a halogen acid to produce an optically active hydroxy acid, equal amounts of the two forms will be produced at a pH 7. Rather the idea is that there is some pH, which we can not now predict, below which one form of the hydroxy acid and above which the other form of the hydroxy acid will predominate in the product. The pH at which equal numbers of the two types of molecules are produced appears to be a specific property of the substances concerned and to be affected greatly by the conditions, especially the temperature. In general the higher the temperature employed the wider the band of pH range which produces inactive products and apparently even at low temperatures the activity does not increase suddenly on either side of this band.

A second objection to Walden's criticism of the Holmberg idea is that in almost all the critical cases cited by Walden the data do not mean what he thinks they mean. To be specific we will cite the first of the six reaction series noted by Walden, that from the work of McKenzie and Humphries[2] on the beta-hydroxy-beta-phenylpropionic acid. This hydroxy acid in alcohol showed a specific rotation of $-18.9°$ for the pure acid and was obtained in each case from a dextro-bromo compound. In the first case the acid stood in water only for five days and the final hydroxy product showed (a)

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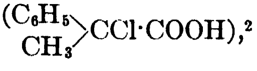
[1] Walden: "Optische Umkehrerscheinungen," 156 (1919).

[2] McKenzie and Humphries: J. Chem. Soc., 97, 125 (1910).

= −7.7°. There is no doubt but that this solution was acid not only with the acid itself but also by virtue of the hydroxyl ions going in to form the hydroxy acid. The second reaction involved 0.0030 mols of the bromo acid and 0.0037 mols of sodium carbonate. The carbonate in this case should be sufficient to neutralize the acid, provide hydroxyl ions, and have left 0.0007 mols for making the system alkaline. The hydroxy acid produced showed −5.5°. In the third reaction 0.003 mols of the bromo acid reacted with 0.003 mols of Ag_2O. This would be just sufficient to form the silver salt and furnish the necessary hydroxyl ions and there would be no reserve silver oxide to keep the solution on the alkaline side. The hydroxy acid resulting showed (a) = −13.7°. In these three reactions we have then; 2.-mildly alkaline (−5.5°), 3.-weakly acid (not alkaline as Walden states) (−13.7°), 1.-decidedly acid (−7.7°). In this case it appears that the acidity of the free acid alone is sufficient to cause some racemization and that a solution which is definitely alkaline would produce dextrorotatory beta-hydroxy-beta-phenylpropionic acid from levorotatory beta-bromo-beta-phenylpropionic acid. It should be borne in mind that strongly acid or alkaline solutions effect a racemization in these reactions and that the inevitable heating used in completing the reactions or separating the products will also tend to a lowered activity of the product which will be variable with the treatment.

This is a typical set of reactions which include those of alpha-bromo-beta-phenylpropionic acid, ($C_6H_5 = CH_2CHClCOOH$),[1] alpha-chloro-alpha-phenylpropionic acid  $\left(\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\rangle CCl\cdot COOH)$,[2] phenylchloroacetic acid into mandelic acid ($C_6H_5CH(OH)COOH$),[3] bromopropionic acid into lactic acid ($CH_3CH(OH)COOH$),[4] and bromoisovalerianic acid.[5]

There are therefore in these cases cited by Walden one or two other exceptions to the general rules but for the most part the reactions which appear to Walden to be exceptions are not really so. It should be noted in passing that, in so far as one may judge from such incomplete and non-comparable data, those halogen acids containing the phenyl group appear to react oppositely to the acids without the phenyl group, for alkaline hydrolysis in the former group is attended by no change of sign or of configuration, while both are present for instance in the malic acid or the lactic acid series. It may later appear that the phenyl-containing compounds are much less sensitive to changes in the hydrogen ion concentration than are those compounds which lack phenyl groups. Possibly this may be connected with the unsaturated character of the phenyl group but at present we have no complete evidence for this.

In the final analysis the hydrolysis of the halogen succinic acids produces molecules of malic acid each of which is optically active and all of which are equally capable of turning the plane of polarized light to exactly the same degree; there are no optically inactive molecules of malic acid. The rotatory power of a sample of malic acid will therefore be determined by the proportions of each form present in the mixture, since any preparation will involve the formation simultaneously of both types of molecules. Thus it is questionable if anyone ever had in hand a pure specimen of either form unmixed with the other, and the best we can do is to take the highest rotatory power observable as that of the pure form. The ratio between the forms of malic acid produced, assuming temperature and other conditions constant and so chosen as to cause a minimum of racemization, will depend upon three principal factors; the original material used, such as the halogen succinic acid, the added hydrolyzing agent, and the medium in which the reaction is carried out. These are all capable of variation and in this paper particular attention has been focussed on the hydrolyzing agent, actually the water serving both as medium and as hydrolyzing agent—possibly with a catalytic factor added.

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[1] McKenzie and Wren: J. Chem. Soc., **97**, 1358 (1910).

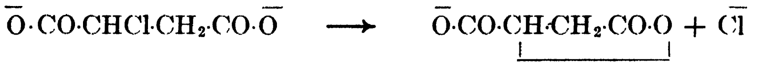
[2] McKenzie and Clough: J. Chem. Soc., **97**, 1022 (1910).

[3] McKenzie and Clough: J. Chem. Soc., **95**, 786 (1909).

[4] Fischer: Ber., **40**, 503 (1907).

[5] Fischer and Scheibler: Ber., **41**, 2894 (1908).

A mechanism of the hydrolysis of the chlorosuccinic acid to malic acid will be found to be somewhat different from that suggested by Holmberg (1927). Accepting a malic acid lactone as the probable intermediate, since the evidence of Holmberg seems clear on that point, the differences in the course of hydrolysis must occur in the hydrolysis of that lactone. The first step will be the formation of the lactone.

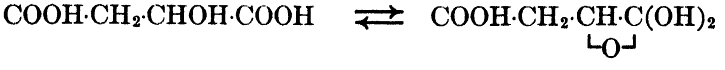


$$\bar{O}\cdot CO\cdot CHCl\cdot CH_2\cdot CO\cdot \bar{O} \longrightarrow \bar{O}\cdot CO\cdot CH\cdot CH_2\cdot CO\cdot O + \bar{Cl}$$

levorotatory anion of chlorosuccinic acid

dextrorotatory anion of the lactone of malic acid

There is nothing in Holmberg's work to establish whether the lactone in question is an alpha or a beta lactone. However, we[1] have previously shown that the fact that l-malic acid is dextrorotatory in concentrated aqueous solution, and under certain other conditions, is due to the fact that it consists of a mixture of tautomeric forms of the formulas:



$$COOH\cdot CH_2\cdot CHOH\cdot COOH \rightleftarrows COOH\cdot CH_2\cdot CH\cdot C(OH)_2$$

normal levorotatory form

ethylene oxide dextrorotatory form

The existence and dextrorotation of this ethylene oxide form was shown by a study of the properties, especially the optically rotatory power, of several related compounds and of the malic acid itself. It is well known that the formation of the lactide from lactic acid, while not commonly believed to be a lactone in the same sense, does involve a change from a chain to an oxygen-containing ring structure and does show the lactide to possess an opposite and remarkable enhanced rotation when compared with the original lactic acid. A similar lactone has been described by Levene and Haller.[2] They reported that a levorotatory gamma-valerolactone ([a] = −27°) was converted by treatment with alkali into the dextrorotatory salt ([a] = +2.7°) and that this salt on addition of sulphuric acid gave the free gamma hydroxyvaleric acid ([a] = +14°). This indicates that the formation of such a lactone as is here postulated would be accomplished without change of configuration and that the lactone would have the opposite sign of rotation to that of the original acid.

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[1] Bancroft and Davis: J. Phys. Chem., **34**, 897 (1930).

[2] Levene and Haller: J. Biol. Chem., **69**, 165 (1926).

Some light might be thrown on the question as to the type of lactone formed from the chlorosuccinic acid by a comparison of similar reactions in the case of alpha and beta-hydroxybutyric acids. Only one type of lactone could be formed in each of these substances while either type could be formed from malic acid. The data are not very extensive, but Fischer and Scheibler[1] did hydrolyze a dextrorotatory beta-chlorobutyric acid at room temperature to obtain a levorotatory beta-hydroxybutyric acid. This is opposite to the effect of silver oxide in the usual tables of the Walden inversion; but further study shows that this hydrolysis was effected by four equivalents of silver oxide per mol of neutralized acid. This excess of silver oxide is larger than any excess reported in this paper and must therefore give the same effects as would have been obtained in an alkaline solution. Therefore the beta-chlorobutyric acid hydrolyzed exactly as the chlorosuccinic acid would under the same conditions. On the other hand the same authors also hydrolyzed some of the same acid in water only (therefore in acid solution) and obtained again a levorotatory beta-hydroxybutyric acid. This experiment was carried out at the boiling point under poor control and resulted in extensive racemization. On their face these two experiments appear to show that in a case in which only beta-lactone could form the course of the hydrolysis is less affected by the acidity of the medium than is the hydrolysis of the chlorosuccinic acid. This would establish the probability that the hydrolysis of the latter acid which is so sensitive to changes in acidity goes through the intermediate formation of an alpha-lactone and not the beta-lactone given by Holmberg. Lacking any comparable data on the alpha-chlorobutyric acid, we are unable to draw any conclusions. Again is emphasized the necessity of carrying out these reactions under very definite conditions, especially with regard to the relative amounts of substances employed.

These considerations indicate that we should accept a lactone as the intermediate step in the hydrolysis, that the rotation of the lactone is in the opposite direction to that of the free chlorosuccinic acid, and that the weight of evidence inclines toward the view that the lactone in question is an alpha lactone of the type we have previously discussed in connection with malic acid. We assume for such an alpha lactone, as Holmberg did for the beta lactone, that no change in configuration takes place in the formation of the lactone from the chlorosuccinic acid.

The way in which the lactone ring breaks down determines whether or not inversion takes place. Disregarding the optical activity for the moment, it is evident that there are two ways in which the lactone ring can break:

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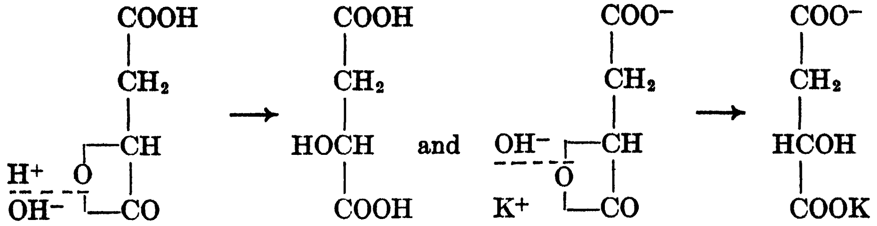
[1] Fischer and Scheibler: Ber., 42, 1227 (1909).



Coming back to the question of optical activity, it is equally evident that the two different ways of reacting would be expected to give two different optically active substances. In the acid reaction as postulated there is no break of the bond between the asymmetric carbon atom and the oxygen. Consequently there can be no inversion and consequently the levorotatory malic acid (the product in acid solutions) has the same configuration as the levorotatory chlorosuccinic acid. Hydrolysis in alkaline solutions produces the oppositely rotatory malic acid showing that the hydroxyl group goes in at some other bond position than the original lactone oxygen bond. Hydrolysis in alkaline solution must produce the salt and is accompanied by inversion.

Conclusions

1. Thirty-five years of study have brought no satisfactory solution of the baffling problems of the Walden Inversion. One important reason for this is the lack of data which are really comparable.

2. Among the first and most widely used substances for the study of the inversion are malic acid and its derivatives. In this series, hydrolysis reactions are governed by the acidities of the solutions and by the varying amounts of suspended hydrolyzing agents.

3. It has been shown that in the conversion of levorotatory chlorosuccinic acid into malic acid, the speed of the reaction is proportional to the hydroxyl ion concentration, and the final products are mixtures of d- and l-malic acids, alkaline solutions favoring the preponderance of the d-malic acid to an extent which, within limits, is proportional to their alkalinity.

4. This is in agreement with the extensive work of Holmberg who postulates an intermediate dextrorotatory malic acid lactone from which acids and alkalies produce oppositely rotatory forms of malic acid.

5. A similar phenomenon has been observed when l-bromosuccinic acid is hydrolyzed in the presence of varying quantities of silver oxide. In the presence of less than 2.7 equivalents of the oxide per mol of acid, the product contains an excess of l-malic acid while more silver oxide causes the product to contain more than 50% d-malic acid.

6. This also confirms the findings of Holmberg and these phenomena throw some light on the failure of the data of the Walden Inversion to agree with some of the other properties of the insoluble oxides, for instance, and on the method which should govern future research in this field.

7. It is pointed out that little more actual progress can be made on this problem until a definite correlation between the rotations and the configurations be established for such simple substances as the halogen succinic acids and malic acid. It is necessary to know when a Walden Inversion takes place in order to study it intelligently.

8. The mechanism is outlined by which the acid hydrolysis of the lactone produces a malic acid of the same rotation and configuration as the original chlorosuccinic acid while the alkaline hydrolysis results in a Walden Inversion, with the oppositely rotatory malic acid. This is opposite to the conclusions of Holmberg and of Levene but in agreement with those of Freudenberg.

Cornell University.

PRINCIPLES DETERMINING THE ARRANGEMENT OF ATOMS AND IONS IN CRYSTALS*

BY M. L. HUGGINS

So many types of crystal structure have been worked out and so much is known concerning the structures of the atoms of which they are composed that it is now possible to determine to a large extent what are the principles determining the arrangement assumed. Such principles are useful in arriving at the structures of other substances. They are also of aid in studies of interatomic forces, and so of molecular structures.

Although some of the ideas to be expressed in this paper originated with the author, many are due to Lewis,[1] the Braggs,[2,3] Goldschmidt,[4] Cuy,[5] Pauling[6] and others.

The first principle to be mentioned is that the influence of an atom on other atoms decreases very rapidly with distance, so that the effect on all but those atoms immediately adjacent to the given atom is almost negligible. Second, atoms of the same kind crystallizing in the same environment, tend to be surrounded similarly. As a result of this, all like atoms or ions are almost invariably surrounded in a similar fashion throughout a given crystal, except of course in such cases as crystals of organic molecules where the surroundings of the atoms were in part determined long before the crystallization.

Combining these two principles, one concludes that the arrangement in a crystal should repeat itself at rather short intervals—that the unit cell should contain relatively few atoms or ions or molecules—and this is known to be the case.

The third principle is that of neutrality. Neglecting the surfaces, which might possess slight excesses of electrical charges, the whole crystal (and hence the unit cell) must be electrically neutral. If a crystal is built up of ions, this determines for simple salts or limits for complex salts the relative numbers of the different kinds of ions, and so the chemical formula.

Another closely related principle may be stated as follows: Negatively charged ions tend to be surrounded by positively charged ions, and vice-versa. No exceptions to this rule are knowm. Both this and the preceding rule are of course derivable from potential theory or from a consideration of the fact that during crystallization an ion would always be drawn toward an ion or group of ions of opposite sign.

One can generalize still further from potential theory and conclude that if a crystal contains anions of more than one kind, those having the greatest negative charge would tend to be in the positions of greatest positive potential,

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* Presented at the Pacific Coast Intersectional Meeting of the American Chemical Society, Eugene, Oregon, June 20, 1930. Contribution from the Chemistry Department of Stanford University.

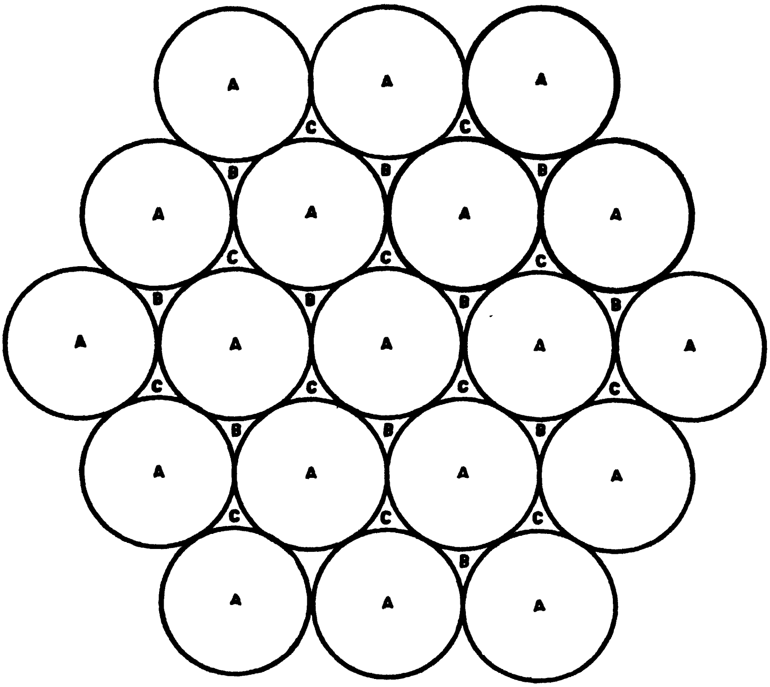

FIG. 1

A layer of spheres in a "close-packed" assemblage. The sphere centers in the next layer are over points marked "B." In the "hexagonal close-packed arrangement" the spheres in the third layer are directly over those in the first, giving the sequence ABABAB. . . .; In the "cubic close-packed arrangement" the sequence is ABCABCABC. . . .

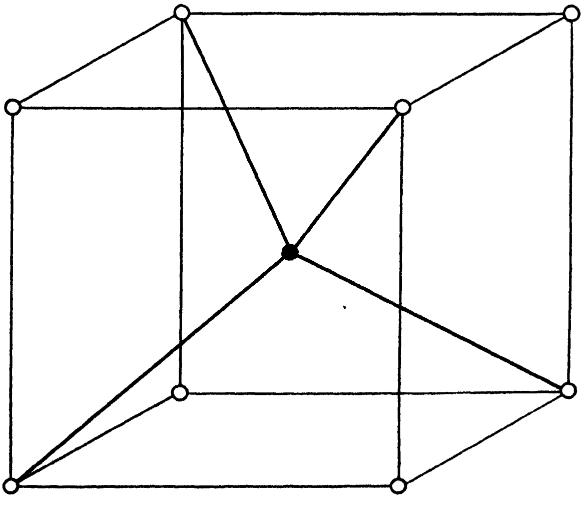

FIG. 2
The unit cube of the CsCl structure.

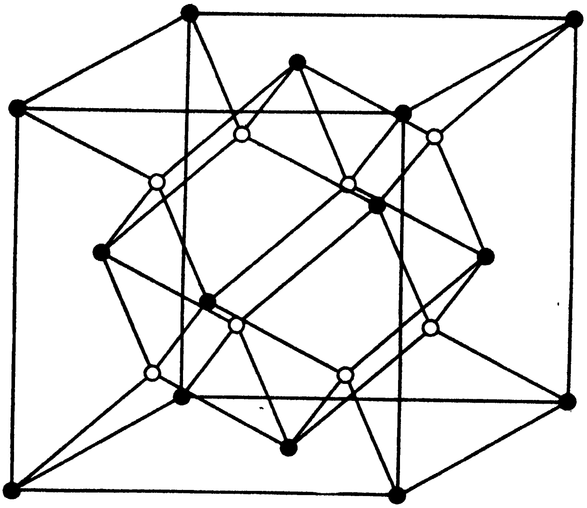

FIG. 3
The unit cube of the CaF_2 structure.

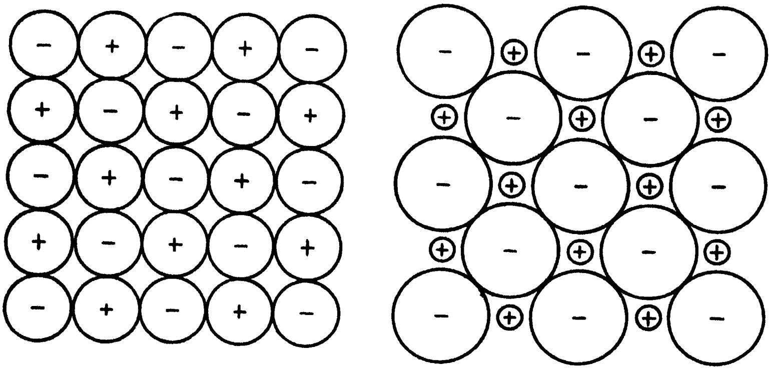

FIG. 4
Illustrating by a two-dimensional analogy, the principle of relative ionic size. This arrangement of ionic centers would be stable for ions of approximately the same size (as shown on the left) but unstable for ions differing greatly in size (as on the right).

those having a smaller charge would tend to be in a position of less positive potential (although still surrounded by positive ions.) This is equivalent to Pauling's "electrostatic valence principle".[6] That something else is involved than potential theory, as applied to point charges, is evident from the fact that the corresponding relationship for cations does not hold.

The next principle to be mentioned is that of "close-packing".[2] It can readily be shown that the most stable arrangements for atoms with spherical force-fields are the same as the arrangements one would get by packing spheres of equal size as closely together as possible,—arrangements in which each atom or sphere is surrounded at equal distances by twelve others (Fig. 1).

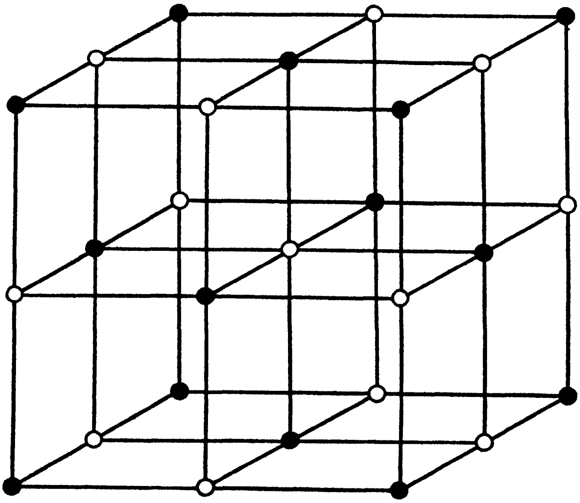

FIG. 5

The unit cube of the NaCl structure. The arrangement of like atoms is the "face-centered cubic" or "cubic close-packed" arrangement. Each atom is surrounded symmetrically by six of the other kind.

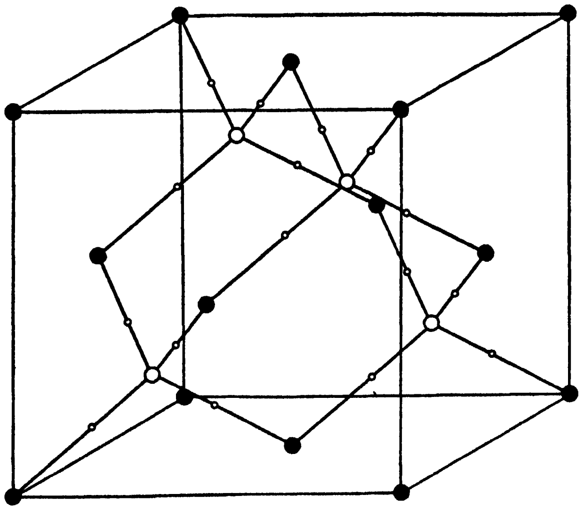

FIG. 6

The unit cube of the ZnS structure. The distribution of the valence electron pairs is indicated by the small circles. Each atom is surrounded symmetrically by four of the other kind. The arrangement of like atoms, considered by themselves, is the same as in the NaCl structure.

The most symmetrical of these arrangements—that of "cubic close-packing" is the one found for solid argon.

The close-packing principle is important also for crystals composed of ions. If the ions are of approximately equal size the closest packing consistent with the rule that each ion is to be surrounded by ions of opposite charge, will be that in which each is surrounded by as many as possible ions of the other kind. If the compound is of the type AB, with equal numbers of A and B ions, this number is eight and the structure is that known as the cesium chloride structure (Fig. 2). In an AB_2 compound there can at most be eight B ions around each A ion and four A ions around each B ion—as in the calcium fluoride structure (Fig. 3).

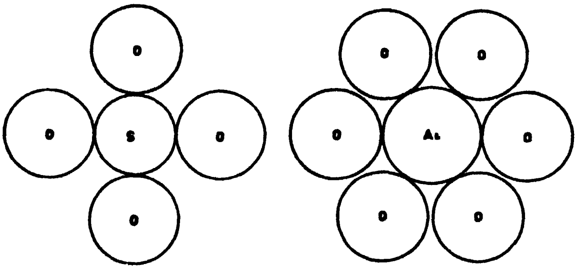

Fig. 7

Illustrating in two dimensions the distribution of oxygen atoms around Si and Al in silicates.

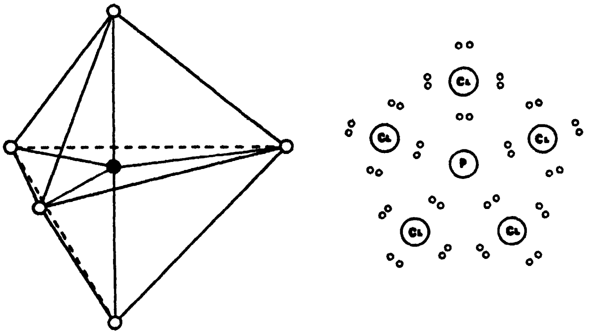

Fig. 8

The probable distribution in space of the atoms in PCl_5, with the corresponding electron formula.

If the ions are of quite different size[4,5,6], arrangements such as these would place like ions too close together as compared with the distances between unlike ions. Closer packing and greater stability is obtained then if the like ions, considered by themselves, form a close-packed lattice. One can roughly approximate the facts by considering the ions as spheres, and assuming that any structure with the spheres of like ions in contact is unstable (Fig. 4). The cesium chloride structure then becomes less stable than the sodium chloride structure (Fig. 5) and that in turn less stable than the zinc sulfide

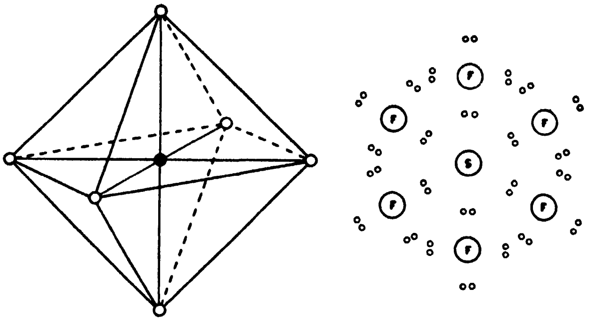

FIG. 9
The probable arrangement of atoms in SF$_6$, with the corresponding electron formula. (This arrangement is the same as that found for SiF$_6^{--}$ in crystals.)

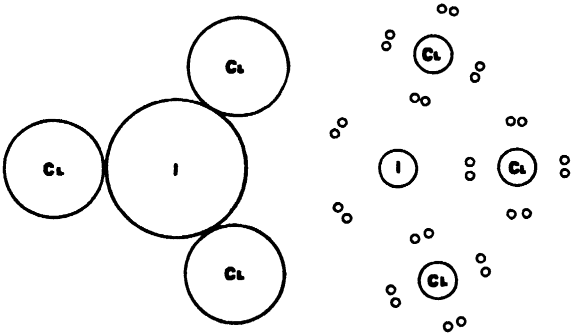

FIG. 10
Probable atomic distribution in ICl$_3$, with the corresponding electron formula.

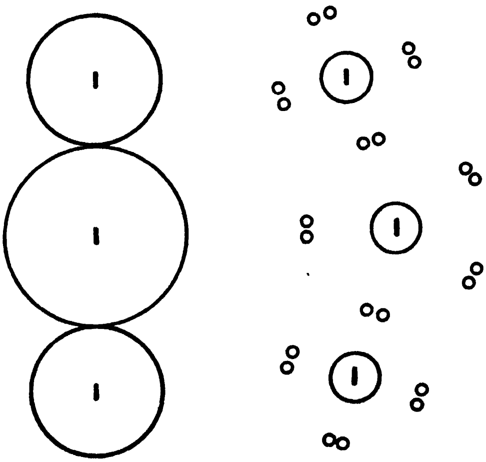

FIG. 11
The arrangement of the atoms in the I$_3^-$ and ICl$_2^-$ ions, with the corresponding electron formula.

structure (Fig. 6) as the ratio of the two radii departs further from one. In both the sodium chloride and the zinc sulfide distributions each ion is equidistant from twelve others of the same sign while in the cesium chloride structure each is equidistant from only eight other like ions.

Similar considerations often determine the number of atoms or ions of opposite sign around a given atom or ion in more complex structures. If the central atom is relatively large compared with the outer atoms, the co-ordination number will be large (say 6 or 8) unless other factors interfere, while if the central atom is relatively small the coordination number must be small, usually four. Thus silicon in silicates seems to be surrounded invariably by four oxygen atoms, while aluminum, somewhat larger, always has six oxygen atoms around it[3] (Fig. 7). The substitution of fluorine for oxygen, however, increases the coordination number of silicon to six, due partly to the smaller size of the fluorine and partly to the decreased repulsion between the negative atoms.

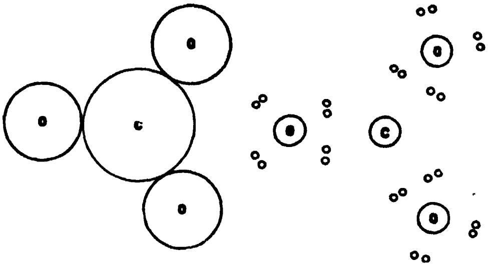

Fig. 12
The arrangement of the atoms in the carbonate and nitrate ions in crystals, with the corresponding electron formula.

Another factor in this and some other cases is the mutual repulsion between the electron pairs of the valence shell of the central atom. If this valence shell has a relatively small radius, as is usually the case for electronegative atoms, only four pairs can surround the kernel without making them too close to each other. However, with more electropositive atoms the valence shells are relatively large and six or more valence pairs can be accommodated. The determining factor then seems to be the repulsion between the surrounding atoms rather than between the electron pairs. Examples of electronegative atoms probably having 5 or 6 pair valence shells are found in phosphorous pentachloride (Fig. 8), sulfur hexafluoride (Fig. 9), iodine trichloride (Fig 10), the tri-iodide and dichloroiodide ions (Fig. 11) and the carbonate and nitrate ions (Fig. 12).

Atoms of electronegative atoms frequently complete their valence shells by sharing electron pairs with other electronegative atoms.[1] From the chemical formula and the number of valence electrons each atom furnishes one can readily calculate the number of shared pairs necessary to give each negative atom its complete shell. Thus in iodine crystals, with seven valence electrons per atom, each atom shares one pair; in selenium and tellurium and probably also sulfur, each atom shares two pairs; in phosphorous, arsenic, antimony and bismuth each atom shares three pairs; and in carbon and silicon each atom shares four (Fig. 13). In the last case the angles between the bonds are those between the lines joining the center of a regular tetrahedron with its corners. If only two or three of the four pairs around an atomic kernel serve as bonds, this angle tends to be somewhat larger, due to the repulsion between the bonded atoms.

As another example may be mentioned "arsenic trioxide", so-called. Each arsenic atom furnishes five valence electrons and each oxygen six. To complete the valence shells each arsenic shares three pairs with oxygens and each oxygen two pairs with arsenic atoms. This determines the empirical formula As_2O_3. The angles between bonds in a molecule of this complexity however would be far from those of a regular tetrahedron and like atoms would be drawn too close together for great stability, so a molecule of the formula As_4O_6, having the structure shown in Fig. 14 is formed.[7] For this molecule the objections mentioned do not hold.

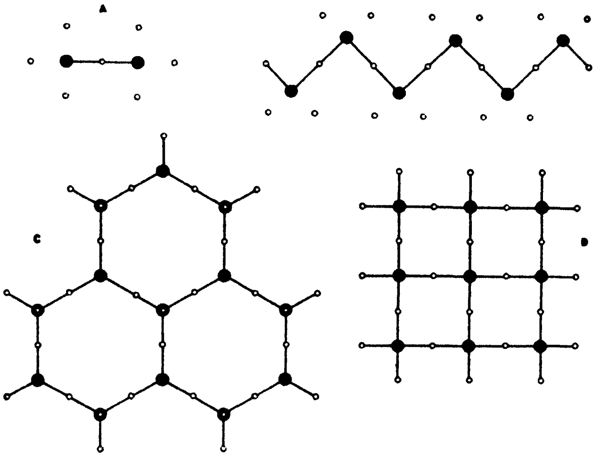

FIG. 13

Illustrating the formation of (A) diatomic molecules as in I_2, (B) string molecules as in Se, (C) layer molecules as in As, and (D) whole crystal molecules as in the diamond, as the result of the tendency of electronegative atoms to complete their valence shells.

The principles thus far mentioned do not in every case determine the orientation of the valence shells of the electronegative atoms or ions with respect to the surrounding electropositive atoms or ions. In some cases the valence electron pairs must be on or near the centerlines joining these atoms, and it would seem reasonable to assume that this would be the case wherever it is structurally possible. In a crystal of the zinc sulfide type for instance, we should expect the sulfur valence tetrahedra to be pointed toward the zinc kernels, giving a tetrahedron also around the latter (Fig. 6). In ferrous disulfide or pyrite, FeS_2, one of the four valence pairs around each sulfur kernel is shared with another sulfur; the others we should expect to be pointing

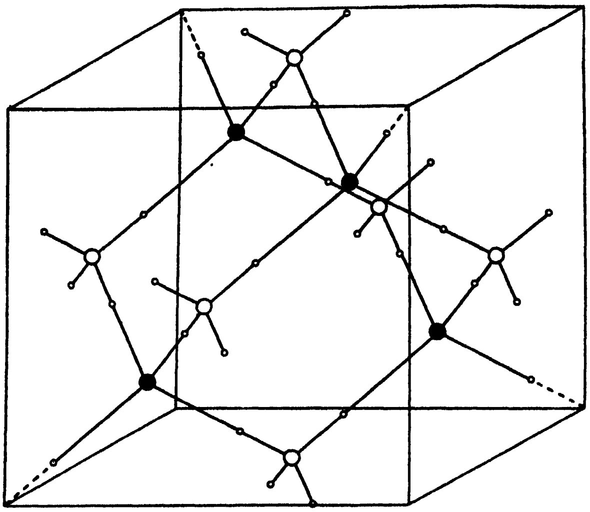

FIG. 14
The arrangement of atoms and of valence electron pairs (small circles) in a molecule of As_4O_6, as found in crystals of "arsenic trioxide." Large dots denote As, large circles O atoms.

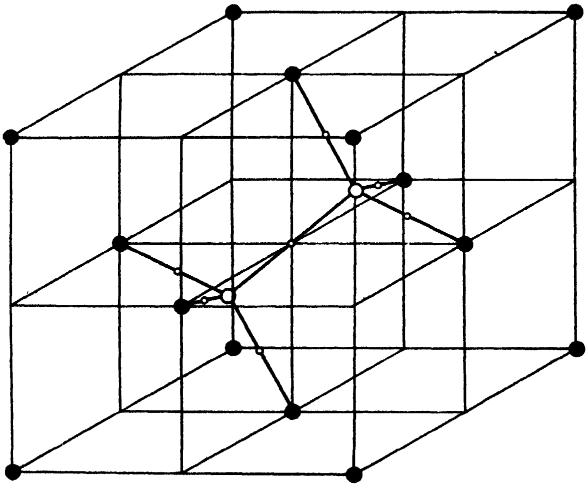

FIG. 15
Showing the arrangement of pairs of valence electrons (small circles) and iron kernels (large dots) around the sulfur kernels (large circles) in a crystal of FeS_2, pyrite. The structure is like that of NaCl (Fig. 5) with Na and Cl replaced by Fe and S_2 groups, respectively.

toward the three neighboring doubly charged iron kernels (Fig. 5) giving an octahedron of six pairs around each of the latter.

One more example will be given. Mercuric iodide consists[8] of layers in which each mercury is tetrahedrally surrounded by four iodines, while each iodine has two mercury atoms adjacent roughly at two corners of a tetrahedron. Orientation of the valence tetrahedra around the iodine kernels toward the mercury atoms gives a similar but larger tetrahedron around each mercury kernel (Fig. 16).

Structures such as this cannot be attributed solely to the attractions between spherical ions. There is apparently also a definite attraction between the kernels of the metal atoms and the valence pairs, resulting usually in tetrahedral or octahedral or cubic valence shells around these metal kernels, depending on the size relationships and structural limitations.

These structural limitations are largely a matter of pure geometry. It frequently happens that all of the tendencies I have mentioned cannot be completely satisfied. Either one of the weaker tendencies remains unsatisfied, as in sodium chloride, where it is impossible for the chlorine valence pairs to be on the atomic centerlines—there being six centerlines and only four pairs —or a compromise is reached, as in corundum, Al_2O_3. Each aluminum wants to be surrounded by six oxygens at corners of a regular octahedron, and each oxygen wants to have four aluminum atoms around it at corners of a regular tetrahedron, but both of these tendencies cannot be satisfied. So actually each aluminum is surrounded by oxygens at corners of a very much distorted octahedron and each oxygen by aluminums at corners of a very much distorted tetrahedron.

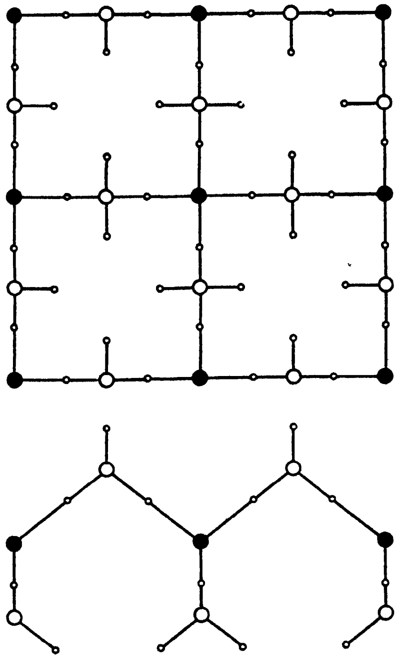

FIG. 16

Showing, in plan and elevation, the arrangement of atomic kernels and valence electron pairs in a layer of the HgI_2 structure. Large dots denote Hg, large circles I atomic centers.

Another principle of which considerable use has been made is that of the approximate constancy of size of an atom in similar structures. What is meant by "size" depends on one's definition or method of calculation, but in spite of differences of opinion in this regard, the idea has proved a most useful one. One can also generalize regarding the relative sizes of different atoms—the effect of increasing the kernel charge or the number of shells in the kernel, etc.—and the differences in size of the same kind of atom in different structures but time will not permit of more discussion of this now.

In presenting these principles no attempt has been made at completeness, nor have they been given in what will probably be their simplest or most useful forms. However if this paper will help to promote a better understanding of the reasons for the various types of crystal structures observed, my object will have been fulfilled. The better these reasons are understood the easier it will be to work out new arrangements and the better we will understand atomic structures, molecular structures and the explanation of properties in terms of these structures.

References

[1] Lewis: "Valence and the Structure of Atoms and Molecules" (1923).
[2] W. H. and W. L. Bragg: "X-Rays and Crystal Structure", Chapter XII (1924).
[3] W. L. Bragg: Trans. Faraday Soc., **25**, 291 (1929).
[4] Goldschmidt: Ber., **60**, 1263 (1927); Z. techn. Physik, **8**, 251 (1927).
[5] Cuy: J. Am. Chem. Soc., **49**, 201 (1927).
[6] Pauling: J. Am. Chem. Soc., **49**, 765 (1927); **51**, 2868 (1929); Z. Krist., **67**, 377 (1928).
[7] Bozorth: J. Am. Chem. Soc., **45**, 1621 (1923).
[8] Huggins and Magill: J. Am. Chem. Soc., **49**, 2357 (1927).

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CHEMICAL ACTION IN THE GLOW DISCHARGE

VI. The Oxidation of Carbon Monoxide

BY A. KEITH BREWER AND PAUL D. KUECK*

The oxidation of carbon monoxide in the glow discharge is of particular interest from two angles. First, it shows the physical state in which the molecules must be placed to become chemically active. Second, it enables the reaction to be studied in steps from the simple non-propagating oxidation, through various lengths of reaction chains, until ignition point is reached.

The cathodic combustion of carbon monoxide has been studied by Finch and Hodge.[1] The investigators conclude the combustion to be determined by ions of both constituent molecules, and that metal atoms sputtered from the cathode are of vital importance in aiding the reaction by overcoming the electrostatic repulsion between the ions.

Recently Finch and Thompson[2] failed to find bands due to ionized carbon monoxide in the cathode zone of an electric discharge in a $2CO/O_2$ mixture. From this they conclude, in contradiction to their previous contentions, that the ionization of carbon monoxide is unnecessary in this reaction. At the same time they state that the failure to find bands due to ionized oxygen is no indication of the absence of these ions.

Lind and Bardwell,[3] studying this reaction in the presence of radon, found that carbon monoxide, when sufficient oxygen was present for combustion, was completely oxidized to carbon dioxide. The maximum ratio of molecules formed to ions reacting was obtained with the combining mixture; from this it was concluded that CO^+ and O_2^+ ions are equally effective. Average values of $M_{(CO+O_2)}/N_{(CO+O_2)} = 6$, or $M_{CO_2}/N_{(CO+O_2)} = 4$, were obtained.

Hunt and Schumb,[4] investigating the carbon monoxide oxygen equilibrium found in general that the rate of oxidation was increased by excess carbon monoxide and retarded by excess oxygen.

The ignition of carbon monoxide oxygen mixtures in the condensed electric discharge has been studied by several investigators[5,6,7] with the apparent agreement that propagation takes place when the ion density in the discharge reaches a definite value depending on the conditions involved.

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* Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, Washington, D. C.

[1] Finch and Hodge: Proc. Roy. Soc., **124**, 303 (1929).

[2] Finch and Thompson: Proc. Roy. Soc., **129**, 314; Finch and Patrick: 656 (1930).

[3] Lind and Bardwell: J. Am. Chem. Soc., **47**, 2675 (1925).

[4] Hunt and Schumb: J. Am. Chem. Soc., **52**, 3152 (1930).

[5] Finch and Cowen: Proc. Roy. Soc., **116**, 529 (1927).

[6] Brewer: Proc. Nat. Acad. Sci., **13**, 689 (1927).

[7] Brewer and Deming: J. Am. Chem. Soc., **52**, 4225 (1930).

Apparatus

The apparatus and general method of procedure employed were described[8] in earlier article appearing in this series.[8,9]

The carbon monoxide used was prepared by the action of formic acid on phosphoric acid. The other gases were purified as described in previous communications.

Results

The oxidation of carbon monoxide follows much more closely the oxidation of hydrogen[9] than it does the oxidation of nitrogen.[10] This is due to the fact that at pressures higher than about one centimeter propogation or chain reactions occur with both hydrogen and carbon monoxide.

An electric discharge in a $2CO/O_2$ mixture at liquid air temperatures gives carbon dioxide as the reaction product, while in the presence of excess carbon monoxide or of neutral gases, carbon suboxide is deposited on the walls of the tube along with carbon dioxide. Carbon monoxide alone dissociates into carbon dioxide and carbon suboxide; the rate is from a quarter to a half that for the oxidation.

Reaction in the Negative Glow. A typical curve for the rate of carbon dioxide synthesis from a $2CO/O_2$ mixture in the negative glow is illustrated in Fig. 1, curve 1. Curves of this type have been taken with discharge tube No. I, at pressures as high as 30 mm, without any further increase in rate than that occurring at 15 mm., and with no tendency towards ignition. Indeed it has never been possible to produce ignition of a $2CO/O_2$ or $2H_2/O_2$ mixture in the negative glow; propagation appears to start only in the positive column.

At pressures below about 9 mm., the rate accelerates in a manner very different from that observed for the previous reactions of this series. It will be noted that the voltage as given by curve IV increases simultaneously with the increase in rate. The rise in voltage at these pressures appears to be due to a change in the normal cathode fall of potential occasioned by the deposition of carbon dioxide and possibly the suboxide on the cathode. Since the rate of ion production is very nearly proportional to the normal cathode fall, the observed increase in synthesis is to be expected.

The effect of current on the rate of synthesis was investigated over the range from 10 ma to 50 ma. The rate was found proportional to the current in tubes I and II over the entire current and pressure range for the negative glow.

The results obtained by varying the ratio of carbon monoxide to oxygen are illustrated in Fig. 2. Curve 2 was taken at 3.5 mm. in tube No. II, equipped with aluminum electrodes, while curve 1 was taken at 10 mm. with iron electrodes in tube No. 1.

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[8] Brewer and Westhaver: J. Phys. Chem., 34, 153 (1930).

[9] Brewer and Westhaver: J. Phys. Chem., 34, 2343 (1930).

[10] Westhaver and Brewer: J. Phys. Chem., 34, 554 (1930).

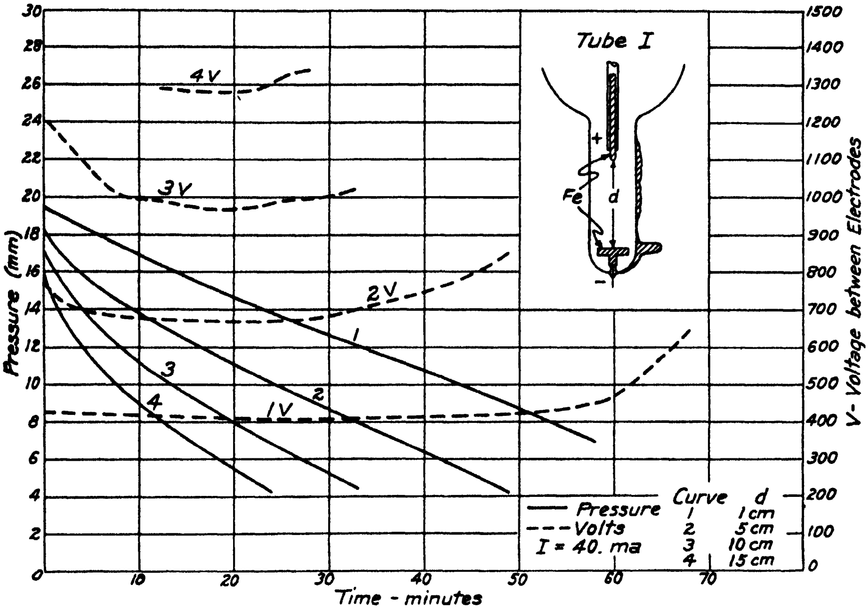
Tube I
+
Fe
d
-
4V
3V
2V
1V
1
2
3
4
Pressure (mm)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
V- Voltage between Electrodes
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
10
20
30
40
50
60
70
Time - minutes
—— Pressure
- - - Volts
I = 40. ma
Curve d
1 1 cm
2 5 cm
3 10 cm
4 15 cm

FIG. 1

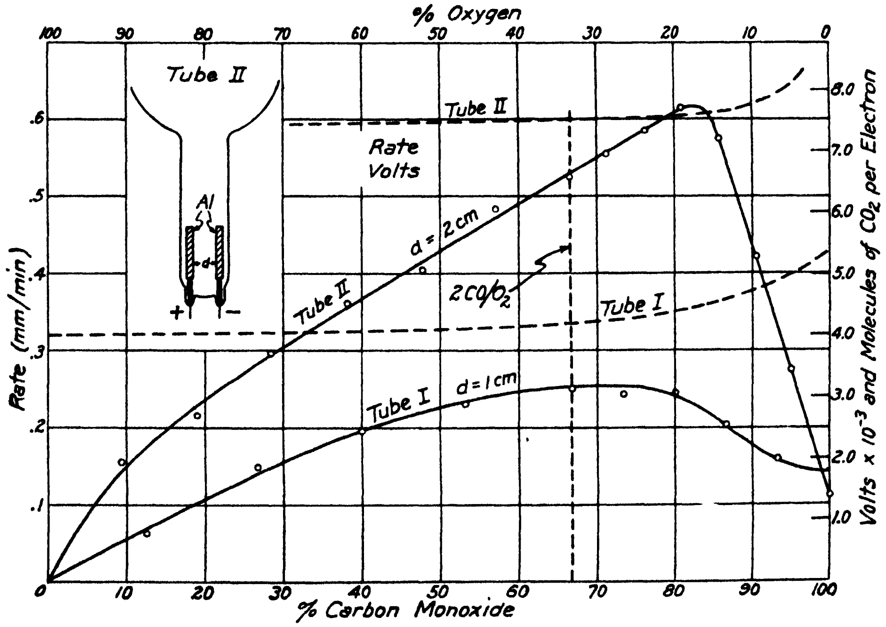
% Oxygen
100
90
80
70
60
50
40
30
20
10
0
Tube II
Al
d
+
-
Tube II
Rate
Volts
d = 2cm
Tube II
2CO/O₂
Tube I
Tube I
d = 1cm
Rate (mm/min)
.1
.2
.3
.4
.5
.6
Volts x 10⁻³ and Molecules of CO₂ per Electron
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
0
10
20
30
40
50
60
70
80
90
100
% Carbon Monoxide

FIG. 2

The difference in rate for curves 1 and 2 is due primarily to a difference in the voltage characteristics of the two tubes rather than to the difference in pressure. The cathode drop in potential was about twice as great for tube II as for tube I.

The effects of excess carbon monoxide and oxygen are shown further in Fig. 3; the results with helium and argon are also given. These data were taken under the same conditions as was curve 2 of Fig. 2.

It will be noted from Figs. 2 and 3 that excess carbon monoxide has an accelerating effect on the rate in all mixtures in which it constitutes less than 80% of the entire volume. Over this composition range oxygen retards the rate almost in proportion to the amount present.

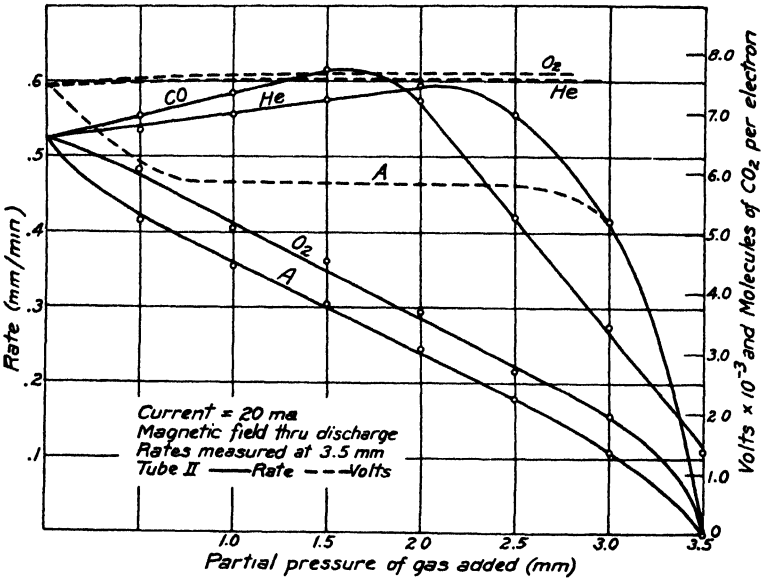

FIG. 3

The fact that excess carbon monoxide shows a more pronounced accelerating effect in curve 2 than in curve 1 of Fig. 2 is due primarily to the proximity of the electrodes to the walls. The cathode in tube II was 1 cm. from the walls, while in tube I it was but 5 mm.; the composition for maximum rate approaches a $2CO/O_2$ mixture as the distance between the cathode and the walls increases.

Reaction in the Positive Column. The reactivity in the positive column for various lengths of electrode separation is given in Fig. 1. Curve 1 gives the rate of synthesis in the negative glow alone. The difference in the slopes of the curves represents the reactivity in the positive column for the length and pressures given.

The rates for different pressures and electrode separations are tabulated in Table I.

A comparison of the values at 8 mm. and 16 mm. shows that the rate increases rapidly with increasing pressure, the longer the positive column the more pronounced the effect. The difficulty involved in starting the discharge made it impossible to determine the rate at pressures just under the ignition point. However, curve 4 of Fig. 1 is started not far below this pressure. Propogation apparently takes place when the rate curve approaches an asymptote parallel to the voltage axis.

TABLE I

Curve	d	6 mm	8 mm	10 mm	12 mm	14 mm	16 mm
1	1.0	.260	.210	.200	.200	.202	.230
2	5.0	.230	.230	.240	.270	.300	.430
3	10.0	.270	.275	.325	.460	.590	.860
4	15.0	.320	.330	.490	.665	.940	1.360

The effect of the current on the rate of synthesis is shown in Fig. 4.

It will be seen that the rate is proportional to the current below 10 mm. pressure, while at higher pressures it becomes slightly less than proportional. These data were taken with tube I, using a 10 cm. electrode separation.

A determination of the effect of excess gases involved considerable difficulty. In the presence of excess carbon monoxide dissociation as well as oxidation occurred, while in the presence of excess oxygen, ozone was formed, along with the carbon dioxide. Additions of inert gases such as nitrogen impeded the oxidation and resulted in the deposition of large quantities of carbon suboxide on the walls. The complicating reactions made it impossible to determine the rate of oxidation under these conditions. The maximum rate, however, was obtained not far from the combining mixture; possibly oxygen accelerated the rate at the higher pressures.

Nature of the Reactants. The characteristics of the time-pressure curves and the proportionality between current and rate are direct indications that the observed reactivity is due to positive ions. The nature of the deposit in the negative glow offers still further evidence of this fact. The carbon dioxide deposit is illustrated in Fig. 1, and is very similar to that obtained in the water reaction. The sharply-defined band of carbon dioxide in the negative glow can not possibly be produced by a diffusion of electrically neutral molecules to the walls; it shows definitely that the molecules synthesized within the glow reach the negatively charged walls as positive ions. The light diffused deposit surrounding the cathode probably comes from the CO_2^+ ions which are neutralized on the cathode or in the gas phase.

A further test of the hypothesis that the chemical action in the negative glow results from positive ions or positive ion clusters neutralized on the walls, was made by placing a positive potential on a tungsten electrode sealed in the side of the tube in the path of the banded deposit. In case no potential was applied to the side electrode the band was quite uniformly distributed around the tube. When a positive potential was applied, only a very light diffused deposit appeared near the electrode, while the deposit on the opposite side was markedly increased. Potentials from 45 to 180 volts were used. The presence of the positive field could have no effect on the deposition of neutral molecules; the very light deposit in the presence of the field, therefore, was probably due to those molecules which had been neutralized on the cathode and in the gas phase. It should be mentioned that these results are doubly effective since the field tends to deflect the electrons towards the side electrode, thus causing an increase in the concentration of positive ions in the adjacent position of the discharge.

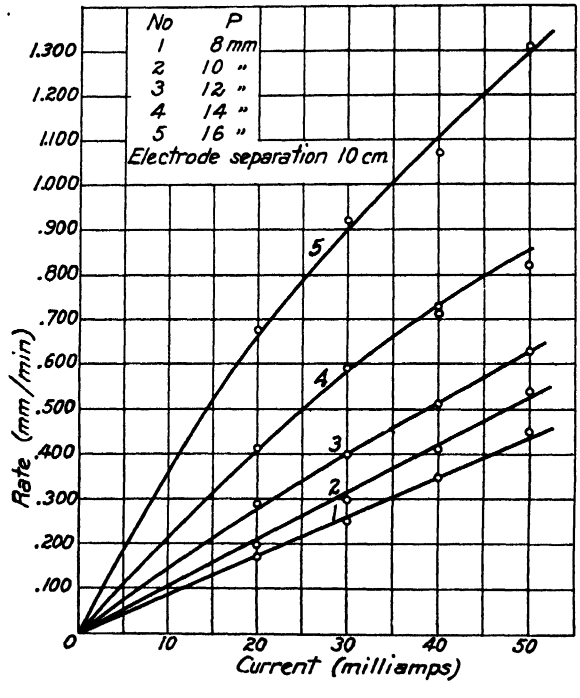

FIG. 4

A similar test was carried out for the positive column by imposing a difference of potential of 180 volts between two electrodes sealed in opposite sides of the tube about two centimeters below the anode. The potential gradient, therefore, was much greater between the auxiliary electrodes than in the path of the discharge. The result differed markedly from that obtained in the negative glow; very little difference could be observed in the thickness of the deposit at the two electrodes, irrespective of the potential applied. Since a test of this type will show only a pronounced difference in the amount of material deposited, all that can be said is that the majority of the molecules synthesized in the positive column strike the walls in the electrically neutral condition. It is possible that the deposit was slightly less at the positive electrode, hence a small fraction of the molecules may have reached the walls as ions or ion clusters.

A Spectrographic Analysis. An examination of the radiation emitted in the negative glow showed, in addition to the bands due to the neutral carbon monoxide molecule, those due to the ionized molecule. With a 60 minute exposure the more intense bands of the first negative group were observed. The approximate wavelengths of the band heads are 2190, 2300, 2325, 2419, 2446, and 2474 Å. These bands were obtained with about the same intensity at pressures from .5 mm. to 10 mm. of mercury.

It should be stated that while these bands show the presence of the excited CO^+ ion, no question exists about the presence of either CO^+ or O_2^+ ions in a $2CO/O_2$ mixture, since the high speed electrons found in the cathode zone will necessarily ionize both gases, the distribution of ions between the two gases being determined by their relative stopping powers and partial pressures.

Computation of Yield

The energy expenditure can best be expressed in terms of the potential through which one electron must drop to bring about the formation of one molecule. In the particular apparatus used the number of molecules of carbon dioxide formed per electron is given by $M = 256 R/I$, where R is the rate of pressure decrease in mm. per minute, I the current in milliamps, and 256 a constant for the 4.3 liter system assumed to be at room temperature.

The yield expressed in terms of electron volts in the negative glow for tube I is given in Table II.

TABLE II

P	I	E	M	V_n
8	40	430	1.34	322
12	40	410	1.28	322
16	40	415	1.47	303
20	40	430	1.53	280

P = pressure in mm.; E = potential drop in negative glow; M = molecules formed per electron of current; V_n = energy in electron volts per molecule.

A maximum value of $V_n = 115$ was obtained with tube II, using a small aluminum cathode 1 cm. from the wall and with a 2 cm. electrode separation. In comparison, the values of V_n for ammonia and for nitrogen dioxide fell between 400 and 450 electron volts. Water, on the other hand, gave a maximum efficiency of $V_n = 41$.

The energy expended per molecule synthesized in the positive column is given in Table III.

TABLE III

P	I	E	M	V_pI	V_pII
6	40	250	.026	975	940
8	40	280	.029	965	915
12	40	330	.122	270	265
16	40	375	.275	137	133

E is the difference in the potential drop through tubes of 5 cm. and 10 cm. electrode separation, while M is the difference in the number of molecules synthesized; V_pI is the yield computed from the above data; V_pII, is the yield computed from similar data taken between 10 cm. and 15 cm. electrode separations.

It will be noted that below 10 mm. pressure the energy expended per molecule is high and very nearly constant. Above this pressure the efficiency of the process increases rapidly.

Discussion of Results

Comparison with Previous Reactions. The results presented above are markedly similar to those stated previously for the oxidation of hydrogen,[9] but exhibit several points of contrast to those obtained in the synthesis of ammonia and nitrogen dioxide. The data show unmistakably that the present reaction, like the others of this series, is purely ionic in character; while it is possible that atoms and excited molecules are chemically active, their reactivity is too slow to be detected in the presence of the fast ionic reaction.

In the negative glow, line 1 of Fig. 1 is very similar to line 1 of Fig. 1 for the water reaction, with the exception that the slight increase in rate occurring above 7 mm. pressure for water now occurs at 15 mm. A further difference is to be seen in the increase in rate below 7.5 mm. This increase, as has been pointed out, results from an increase in the normal cathode fall of potential and does not represent an enhanced reactivity at these pressures. In contrast to the increased rate observed above, 7 mm. and 15 mm. for H_2O and CO_2, respectively, it should be mentioned that recent experiments have shown the rate of synthesis of NH_3 to be constant from 40 mm. to about 0.2 mm. The reactivity in the positive column is very similar to that observed for H_2O, as can be seen by comparing curves 2, 3, and 4 of Fig. 1 in this paper with curves 3 and 4 of Fig. 1 of the preceding paper.[9] Both reactions show a rate that is independent of the pressure up to some particular pressure above which the rate increases rapidly to the ignition point. This is again in direct contrast to the ammonia reaction where no such enhancement was observed, the phenomenon being found only in cases where ignition is possible.

The Nature of the Reaction. The results which have been presented show very clearly that the molecules synthesized in the negative glow reach the walls carrying a positive charge. This means either that the molecules are built around positive ions as reaction centers, or that, if the molecules are formed from neutral reactants (for instance, $O + CO = CO_2$) all the molecules become ionized before reaching the walls. The evidence, as has been stated before, supports the former contention, namely, that positive ions are the reaction centers. The low current density combined with the rapid wall neutralization, as shown by the narrow banded deposit, indicates that the probability of a neutral carbon dioxide molecule being ionized in the discharge is small; complete ionization, therefore, is highly improbable.

The fact that most of the molecules synthesized in the positive column reach the walls in the neutral form necessitates either an entirely different mechanism for this region of the discharge, or the conditions must be such that a gas phase neutralization of the ions is possible. It seems improbable that the mechanism of reaction should be different, since below 10 mm. pressure the characteristics of the reactions are identical to those of the negative glow, i.e., the rate is independent of the pressure and proportional to the current, and the effect of excess gases is the same in the two regions of the discharge. On the other hand at the pressures where the reactivity in the positive column was studied (4 mm. to 30 mm.) a rapid gas phase neutralization of the ions—is expected from the O_2^- ions present under these conditions.

The Presence of a Chain Reaction. A comparison of line 1 of Fig. 1 for the negative glow with lines 2, 3, and 4 for the positive columns shows that at pressures below about 8.0 mm. a simple ionic reaction exists in both cases. The energy expended in electron volts per molecule changes but little at any point in the negative glow and is also very nearly constant at the lower pressures in the positive column. At pressures above 8 to 10 mm., however, the energy expended in the positive column drops rapidly with increasing pressure until ignition takes place. This is clearly the transition of the simple ionic reaction into the chain reaction found in ignition. A similar condition exists for the oxidation of hydrogen where chains can be detected at pressures as low as 5.0 mm.

The most reasonable interpretation for these observations is that given in the previous communication[9] for the oxidation of hydrogen. Chains are detectable only where the deposits show the CO_2 to reach the walls in the neutral and not the charged form, the activity of the ions ceasing upon striking the walls. The head of the reaction chain, therefore, is either an ion, some product of the ionic neutralization, or some new active state produced at the higher pressures. The latter possibility seems small since the chain is clearly an outgrowth of the simple ionic reaction and since it is not observable in the negative glow. It is more difficult to distinguish between the first two possibilities, although the evidence appears to favor the former hypothesis since chains were not observed by Lind using α rays, and since it is doubtful if any active state such as atomic oxygen could be produced by neutralization, that is not produced throughout the discharge by electron impact.

Relative Reactivity of the Ions. A high-speed electron on entering the negative glow from the Crookes' dark space, produces both CO^+ and O_2^+ ions. It becomes of interest, therefore, to contrast the reactivity of these two ions. In referring to Fig. 2, it may be seen that oxygen retards the rate almost in proportion to the amount present, while carbon monoxide accelerates the rate in all mixtures containing more than 15% oxygen. This fact may also be seen in Fig. 3, where the addition of excess oxygen has practically the same retarding action on the rate as does added argon. The normal cathode fall of potential being slightly lower in argon than in oxygen causes the observed difference in the effects of these two gases.

The conclusion to be drawn from the above results is that the reaction is initiated by the CO^+ ions, and that O_2^+ ions are comparatively inert. In the water reaction it will be recalled that the reactivity was attributed primarily to H_2^+ ions and that O_2^+ ions appeared inert at pressures below 7mm. The same interpretation holds in the negative glow for the present reaction. CO^+ ions exhibit reactivity over the entire pressure range, while O_2^+ ions appear inactive below 15 mm. pressure in the negative glow.

It is now possible to estimate the minimum number of collisions that an O_2^+ or a CO^+ ion must make in a $2CO/O_2$ mixture for the reaction to take place, from the breaks in the time-pressure curves and from the distance between the cathode and the walls. This value for CO^+ is of the order of 40 collisions in contrast to 20 for H_2^+ ions. Similarly, assuming the reactivity of O_2^+ ions to begin at 15 mm. about 2200 such collisions will be required for reaction, as compared to 1000 collisions for O_2^+ ions in a $2H_2/O_2$ mixture.

The M/N Ratio. The M/N ratio, i.e., the number of molecules synthesized per ion, may be determined from the value of M as given by the rate, and from N, the computed number of ions formed per electron of current. M may be measured accurately, but N involves considerable speculation. In evaluating N the negative glow and the positive column will be discussed separately.

Heretofore in considering the rate of positive ion formation in the negative glow the positive ion current has been neglected. Recent experiments have shown the positive ion current reaching the cathode contstitutes but a small per cent of the total current at pressures above 1 mm., hence the above assumption seems approximately correct. It has been assumed, further, that the energy of an electron entering the negative glow from the Crookes' dark space is very nearly that of the normal cathode fall of potential. The number of ions formed per electron has been computed from the extrapolated results of Langmuir and Jones[11] on the ionizing efficiency of various speed electrons. Recent tests with a large number of cathode materials have shown that the rate is roughly proportional to the normal cathode fall; this is in line with the above method of computing N. It should be mentioned in this connection that the rate is unaffected by changes in voltage occasioned solely by changes in pressure; this fact has also been observed by Linder[12] studying organic reactions under somewhat similar conditions. On the other hand, changes in voltage which result from changes in the electrode material or from a deposit forming on the cathode produce very nearly proportional changes in the rate.

It is not possible to obtain more than the order of magnitude for the value of N in the present case, since the ionizing efficiency of an electron in oxygen and carbon monoxide is not known. α ray studies show these gases to be similar to nitrogen, hence the total number of ions per electron will be considered the same as for nitrogen. Since the stopping powers of the two gases are very nearly identical, the distribution of ions between the gases is proportional to their relative concentration.

In Fig. 2, line 2, it will be seen that 6.7 molecules of carbon dioxide are formed per electron of current, while the potential drop is 750 volts. A 750 volt electron produces about 5.5 positive ions, or 3.6 CO^+ ions for the combining mixture. This value, in the absence of accurate data, is necessarily an approximation, but is probably correct to within a factor of two. From these considerations the number of molecules formed per ion is $M/N = 6.7/3.6 = 1.85$. This is very close to $M/N = 2$. This value, therefore, can be considered as representing the order of magnitude of the ratio of molecules formed to ions reacting. Lind, using α rays, gives $M/N = 4$, but it does not seem probable that such a high efficiency exists under the present conditions.

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[11] Langmuir and Jones: Phys. Rev., (2) **31**, 357 (1928).

[12] Linder: Phys. Rev., (2) **36**, 1375 (1930).

A Possible Mechanism. The data presented above yield a fairly accurate picture of the processes involved in the reaction mechanism. The fact that the carbon dioxide synthesized in the negative glow reaches the walls carrying a positive charge is definite evidence in favor of the ion cluster theory.

The conditions imposed by the character of the reaction in the negative glow are satisfied by the following equation:

$$CO^+ + CO + O_2 = (C_2O_4)^+ \text{ (wall)}$$

also for high pressures,

$$O_2^+ + 2CO = (C_2O_4)^+ \text{ (wall)}$$

Gas phase neutralization is possible in both the negative glow and the positive column, according to the equation

$$CO^+ + CO + O_2 = (C_2O_4)^+ \quad \text{(ion cluster)}$$
$$(C_2O_4)^+ + O_2^- = 2CO_2 + O_2$$

The simple cluster reaction just presented readily develops into the ionic chain mechanism postulated for the positive column, if neutral carbon dioxide splits out of the ion cluster, leaving the ion free to act as a further clustering center. The fact that oxidation is greatly retarded and decomposition increased in the positive column when nitrogen is present is an argument in favor of the ion cluster chain; the addition of neutral molecules to the cluster appears to break the reaction chain.

The writers wish to express their thanks to Dr. C. H. Kunsman for the interest he has taken in these researches, and to Mr. J. W. Westhaver, for his contributions to this paper.

Summary

The rate of oxidation of carbon monoxide in the negative glow is very nearly independent of the pressure over a wide range. It is proportional to the current, and is accelerated by excess carbon monoxide and retarded by excess oxygen almost in proportion to the amount added.

In the positive column the rate is proportional to the current and independent of the pressure below 10 mm. At higher pressures it increases rapidly to the ignition point. Ignition, apparently, starts only in this region of the discharge.

The carbon dioxide synthesized in the negative glow reaches the walls as positive ions. In the positive column, on the other hand, it is deposited largely as neutral molecules.

The bands of the first negative group for carbon monoxide appear with about equal intensity over a wide pressure range.

The data are interpreted as indicating a simple ion cluster mechanism for the negative glow, and an ion chain mechanism for the positive column. CO^+ ions appear much more effective than O_2^+ ions in initiating the reaction; a comparison of the reactivities of the two ions is given.

An estimation of the rate of production of positive ions in the negative glow yields a ratio of $M/N = 2$, for the number of molecules synthesized to positive ions formed.

CHEMICAL ACTION IN THE GLOW DISCHARGE

VII. The Dissociation and Oxidation of Methane

In the previous papers of this series it has been shown that the chemical action in the glow discharge is initiated primarily, if not entirely, by positive ions; an Electrochemical Equivalence Law[1] comparable to Faraday's Laws for Electrolytes has been proposed for the relationship existing between the current flowing and the amount of material reacting.

The present paper, which concerns the dissociation and oxidation of methane, is of interest from several angles: it furnishes another test for the Equivalence Law mentioned above; in connection with the results obtained in the oxidation of hydrogen it offers a comparison of the reactivities of free and combined hydrogen; the complexity of the reaction products obtained from the dissociation of methane throw considerable light on the steps involved in the reaction process; and lastly it is an addition to the large amount of work already done on the dissociation and oxidation of methane by α rays and in the corona discharge.

The effect of α radiation on methane has been studied in detail by Lind and Bardwell.[2] The results show that the reaction takes place at room temperature without an appreciable change in pressure, methane being converted in almost equal proportions into ethane and an unsaturated oil having the empirical formula C_nH_{2n}; other saturated hydrocarbons are formed in amounts decreasing with the complexity of the molecule.

Lind and Glockler[3] have recently shown that methane undergoes similar changes when acted on by α rays and by the semi-corona discharge. In both cases hydrogen is liberated and saturated hydrocarbons formed in amounts decreasing with the length of the carbon chain. A liquid phase having the general formula C_nH_{2n} also appears.

The condensation of several normal hydrocarbons heavier than pentane has been found by Linder[4] to obey the Electrochemical Equivalence Law mentioned above.

The oxidation of methane by α radiation has been shown by Lind and Bardwell[5] to proceed completely to carbon dioxide and water. The observed value for the ratio of molecules synthesized to ions formed is $M/N = 4.4$.

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* Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, Washington, D. C.

[1] Brewer and Westhaver: J. Phys. Chem., 33, 883 (1929).

[2] Lind and Bardwell: J. Am. Chem. Soc., 48, 2335 (1926).

[3] Lind and Glockler: J. Am. Chem. Soc., 52, 4450 (1930).

[4] Linder: Phys. Rev., (2) 36, 1375 (1930).

[5] Lind and Bardwell: Science, 62, 422 (1925).

Apparatus

The apparatus and method of procedure are the same as were employed in the oxidation of hydrogen[6] and of carbon monoxide.[7]

Commercial methane, about 96% pure, was further purified by fractional distillation at liquid air temperatures. The other gases used were purified as described in the previous communications.

Results

The Dissociation of Methane. Methane underwent a dissociation and subsequent condensation in the negative glow at liquid air temperatures without a detectable change in pressure. The removal of the liquid air, after the discharge had been in operation for some time, showed an increase in pressure in the enclosed system approaching 50%. The original pressure was again obtained when the tube was brought to liquid air temperatures.

An analysis of the spectrum of the residual gas showed it to be hydrogen. A detailed study of the condensate was made after the residual gas had been pumped off. When the system was well evacuated, the liquid air level was lowered and the rate of evaporation of the condensed product was measured by observing the increase in pressure with time. The points all fell on a smooth curve, indicating the presence of only a single component.

An idea of the vapor pressure of the condensate was obtained by cooling the tube with dry ice dissolved in alcohol. No decrease in pressure except that due to temperature was observed when the system was cooled to −80°C, while a total clean-up took place at −180°C. The vapor pressure, therefore, was above 4 cm. at −80°C.

It is now possible to identify the condensate from the vapor pressures and from the pressure change. The only hydrocarbons possessing the necessary vapor pressures are ethylene and ethane, possibly propylene and propane. The fact that dissociation takes place at liquid air temperatures without a change in pressure necessitates that for every molecule of methane condensed a molecule of hydrogen is freed. This limits the reaction product to either ethylene or propylene. The pressure increase observed upon evaporation of the condensate shows it to be ethylene. A further confirmation was made by passing bromine into a tube containing a sample of the condensate; the bromine was decolorized almost instantly, showing the hydrocarbon to be unsaturated.

The conclusion to be drawn from the above observations is that methane in the glow discharge operating at liquid air temperature is converted quantitatively into ethylene and hydrogen. This is in distinct contrast to the α ray reaction at room temperature where the products are ethane and several higher saturated hydrocarbons, as well as a liquid unsaturated condensate.

The number of molecules formed per electron of current was determined by running a discharge of 20 m.a., for three minutes and then pumping off the hydrogen and undecomposed methane. When the liquid air was removed the pressure in the 4.3 liter static system at room temperature was 0.465 mm. This is equivalent to 3.1 molecules of ethylene synthesized per electron.

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[6] Brewer and Westhaver: J. Phys. Chem., 34, 2343 (1930).

[7] Brewer and Kueck: J. Phys. Chem., 35, 1281 (1931).

The electric discharge in methane at room temperatures differed materially from the cooled discharge in that a large amount of grayish yellow deposit formed on the walls. This material proved inert to the ordinary solvents and was probably the same substance observed by Lind and Glockler in the semi-corona discharge.

The Oxidation of Methane in the Negative Glow. A $CH_4/2O_2$ mixture is converted entirely to water and carbon dioxide in the negative glow. The characteristics of the reaction are similar to those previously studied in this series in that the rate is independent of the pressure and is directly proportional to the current. It, therefore, obeys the Electrochemical Equivalence Law for the glow discharge, namely:

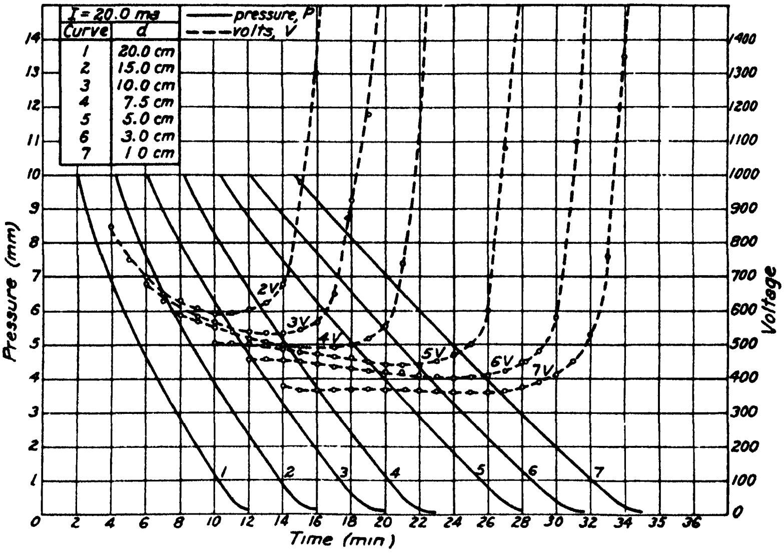

FIG. 1

$$dP/dt = \alpha I$$

where P is the equivalent pressure of the reaction product, α a constant for the reaction, and I, the current.

Line 7 of Fig. 1 is characteristic of the results obtained with a $CH_4/2O_2$ mixture. The discharge tube was of the type illustrated in Fig. 4, the separation of the iron electrodes being 1 cm.

The time-pressure curves starting at any pressure below 10 mm. were very nearly straight lines down to 0.1 mm., where the reaction ceased abruptly. Runs starting above 10 mm. showed a variation in rate with pressure, although the effect was negligible below 25 mm. The formation of ozone along with the regular reaction gave an enhanced rate at the higher pressures, while the decrease in rate at the lower pressures resulted from insufficient oxygen. It is significant to note that while a $2H_2/O_2$ mixture cooled in liquid air yielded about 20% hydrogen peroxide at all pressures, the $CH_4/2O_2$ mixture gave a clean-up to 0.1 mm. for all runs starting under 15 mm. pressure; water and carbon dioxide, therefore, are the only oxidation products formed.

The effect of varying the ratio of methane to oxygen is shown in Fig. 2. It will be noted that the maximum rate occurs for a 1:1 and not for a combining mixture. The rate curve resembles more nearly the curve for the oxygen-nitrogen mixture, than it does the corresponding curves for water and carbon dioxide, in spite of the fact that these two substances are the sole reaction products. This indicates that the combining ratio of the reacting molecules, as well as their chemical nature, determines the rate.

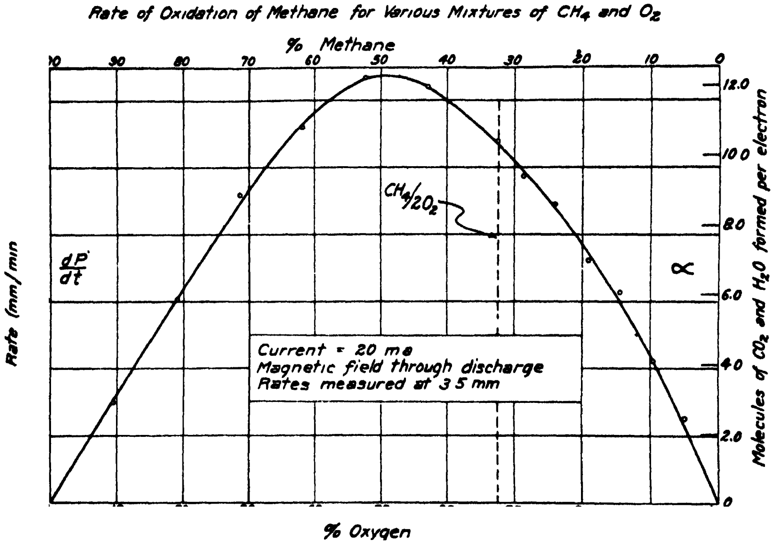

FIG. 2

The effect on the rate caused by the addition of various gases to the $CH_4/2O_2$ mixture is shown in Fig. 3. The data presented in Figs. 2 and 3 were taken with a tube of the type shown in the inset, aluminum electrodes being used.

These curves are in general quite similar to those obtained for the previous reactions. It is of interest to note that in all the oxidation reactions studied

TABLE I

P	dR	dV	dM/e	V_p
10	.68	230	13.10	17.7
8	.35	210	6.72	32.0
6	.26	130	5.00	38.5
4	.09	75	1.74	43.0

the additions of oxygen and argon produce similar effects, both decreasing the rate almost in proportion to the amount added. The accelerating effect of excess methane is illustrated in Figs. 1 and 2. The curves for added helium and argon are markedly different, in that helium has an accelerating effect even when presented in relatively large amounts; the rate for 75% helium is the same as for the combining mixture. The fact that the maximum is the same for excess helium as for excess methane suggests the possibility that helium transfers its activity to the methane.

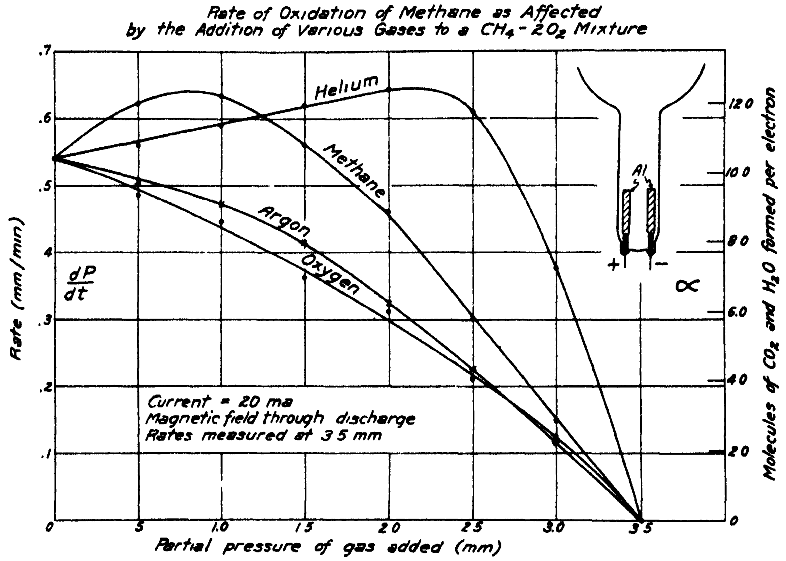

FIG. 3

Oxidation in the Positive Column. The effect of the electrode separation on the rate of synthesis in a $CH_4/2O_2$ mixture is shown in Fig. 1. All curves show a clean-up to 0.1 mm., indicating that carbon dioxide and water are the only reaction products formed.

The effect of the positive column can be seen from the character of the curves. Beginning with curve 5 for 5 cm. electrode separation, the progressive acceleration in rate at the higher pressures is indicative of a positive column. The rate of synthesis in the positive column is independent of the pressure below about 5.5 mm., as shown by curves 1, 2, and 3, while above this point the rate increases with increasing pressure. A similar effect was observed for the oxidation of hydrogen and of carbon monoxide; the synthesis of ammonia, on the other hand, showed no acceleration in the positive column at the higher pressures.

The effect of pressure on the efficiency in the positive column is shown in Table I.

P is the pressure; dR is the difference in rate for 20 cm. and 15 cm. electrode separation; dV is the difference in the corresponding voltages; dM/e is the difference in the number of molecules synthesized per electron of current; V_p is the electron volts necessary for the synthesis of one molecule.

Table I shows very clearly that energy expended per molecule synthesized decreases rapidly with increasing pressure.

The rates and voltages at 4 mm. pressure for various electrode separations are tabulated in Table II.

TABLE II

Curve	d	I	R	$V_{(min)}$
1	1.0 cm.	20 m.a.	.500	360
2	3.0	"	.515	405
3	5.0	"	.550	445
4	7.5	"	.660	492
5	10.0	"	.715	535
6	15.0	"	.800	595
7	20.0	"	.890	670

d is the electrode separation, I the current, R the rate in mm/min., and V the potential drop between the electrodes.

The reactivity in various portions of the discharge is illustrated in Fig. 4. The electrode separation is plotted against the number of molecules synthesized per electron of current in the outer circuit. All values given are for the number of molecules formed per centimeter of tube length; i.e., with an electrode separation of 1 cm., a yield of 9.6 molecules per electron was obtained, et cetera.

It will be seen that the synthesis takes place primarily in the negative glow. The dark spaces are relatively inert, while the reactivity in the positive column is small and very nearly uniform.

Discussion of Results

The Decomposition of Methane. The decomposition of methane in the negative glow takes place according to the equation

$$2CH_4 \xrightarrow{e} C_2H_4 + 2H_2$$

The formation of ethylene as the only hydrocarbon is significant in that it shows the reaction process to be a very simple one. Lind and Glockler[3] observed the formation of most of the light saturated hydrocarbons, as well as unsaturated oils, in the uncooled electric discharge wherein the reaction products were not removed as fast as formed. As a result of finding only ethylene in the present experiment, it must be concluded that the complex molecules obtained in the hot discharge are due entirely to secondary reactions about ethylene.

The character of the results is such that there can be no doubt that this reaction, like those studied before, is initiated entirely by the positive ions formed in the discharge. An idea as to the simplicity of the ionic processes involved can be obtained from the ratio of molecules of ethylene synthesized (M) to CH_4^+ ions formed (N).

The value of N can be computed from the ionizing efficiency of an electron possessing an energy equal to the observed normal cathode fall of potential. Unfortunately the ionizing efficiency in methane is not known, although the work of Hughes and Klein[8] shows this gas to be very similar to nitrogen and hydrogen. Assuming the value to be the same as that of hydrogen, a 350 volt electron should produce about 3.5 positive ions. At the same time 3.1 molecules of ethylene are formed. This gives a ratio of $M/N = 3.1/3.5 \doteq 1$. It seems reasonable that the observed ratio should be less than one, since neither the positive ion current nor the possibility of H_2^+ ions are taken into account.

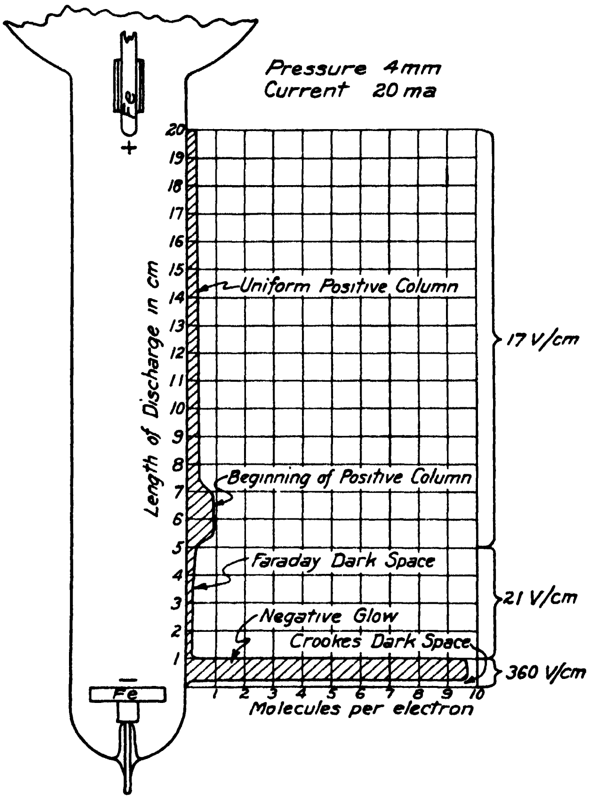

FIG. 4

The reaction process may be expressed by the following equation.

$$(CH_4)^+ + CH_4 \longrightarrow (C_2H_4)^+ + 2H_2$$

In the absence of rapid wall neutralization and especially at high pressures, it is to be expected that $(C_2H_4)^+$ might react with hydrogen to form $(C_2H_6)^+$ or with ethylene to form the condensation products observed by Lind and Glockler.

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[8] Hughes and Klein: Phys. Rev., (2) 23, 450 (1924).

The Oxidation of Methane. The oxidation of methane presents no marked contrast to the reactions discussed in the preceding papers. The results, therefore, necessitate the same general interpretation.

The rate of reaction, as shown in Fig. 3, is accelerated by excess methane and is retarded by excess oxygen almost in proportion to the amount present. The inference to be drawn is that the reaction takes place primarily around the CH_4^+ ions and that O_2^+ ions are relatively inert. *The fact that the activity is due to CH_4^+ ions is of particular interest since in every case so far studied the ions of the reacting gas having the higher ionization potential show the greater activity.* The ionization potential of methane, as given by Glockler, lies between 14.4 and 15.2 volts, while that of oxygen is 14.1 volts.

The failure to detect hydrogen peroxide in the reaction product at pressures below 10 mm. at least, indicates that the oxidation is not preceded by a dissociation into ethylene and hydrogen, the oxygen then reacting with these two products separately, since the reaction of hydrogen and oxygen alone at liquid air temperatures results in the formation of at least 20% peroxide. It is evident, therefore, that the oxidation takes place directly in the ion cluster without the necessity of dissociation. Since the experiment on the dissociation of methane showed that two molecules of hydrogen readily split out of a $(2CH_4)^+$ cluster it seems possible that water might be expected to split off from a $(2CH_4O_2)^+$ cluster before it becames neutralized on the walls.

The Activity of the Ions. The readiness with which the reaction takes place around a CH^+_4 ion may be seen from the minimum pressure to which the reaction can be carried. Line 1 of Fig. 1 shows that the rate of reaction, while independent of pressure over a wide range, abruptly drops to zero at 0.1 mm. Assuming an ion must travel 1 cm. before reaching the walls, and using kinetic theory values for the collision frequency, the minimum number of collisions a CH_4^+ ion must make for the reaction to take place comes out to be about 15. This value is a very rough approximation, however, since the temperature of the gas near the cathode may be several hundred degrees centigrade, while near the walls it approaches that of liquid air. Again, if the cluster mechanism is correct and an ion grows in size with successive collisions, the collision frequency will not remain constant but will increase with the complexity of the cluster. The value of 15, therefore, gives only the order of magnitude for the minimum number of necessary collisions. A similar estimation in previous reactions was $H_2^+ = 20$, and $CO^+ = 40$.

The M/N Ratio in the Negative Glow. The number of O_2^+ and CH_4^+ ions formed per electron with an energy equal to the normal cathode fall of potential is very close to 4, as deduced from the extrapolated values of Langmuir and Jones.[9] Since the stopping power of methane does not differ materially from that of oxygen, the ions will be divided according to the ratio of the gases present. Thus, about 1.4 CH_4^+ ions will be formed per electron. In Fig. 3 it will be seen that 10 molecules of water and carbon dioxide are synthesized for each electron of current. The number of molecules synthesized per ion is, therefore, $M/N = 10/1.4 = 7.1$. Lind, using α rays, obtained a value of $M/N = 4.5$.

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[9] Langmuir and Jones: Phys. Rev., (2) **31**, 357 (1928).

The ratio just obtained seems excessively high, in spite of the fact that the rate is fast and the voltage low. Of course, the value of N may easily be in error by a factor of 2, since the ionizing efficiency of an electron is not known accurately in either methane or oxygen; α rays, however, show both gases to be similar to nitrogen. Again, the assumption that O^+_2 ions are completely ineffective may be in error, since a comparison of the methane curve in Fig. 3 with similar curves for hydrogen, carbon monoxide, and nitrogen, with oxygen, shows that excess methane accelerates the reaction only over about half the pressure range observed for the other gases. Thus, there is a possibility that O_2^+ ions are more effective in this case than in the previous reactions.

The M/N Ratio in the Positive Column. An estimation of the number of ions formed in the positive column entails a large amount of uncertainty, since the amount of energy expended in ionization as well as the distribution of ions between the reactants are both unknown. The electrons in this region of the discharge are generally conceded to possess a Maxwellian distribution of velocity, the average energy being far below that necessary for ionization; much of the energy, therefore, is spent in processes other than ionization. Again, since the energy of the electron seldom, if ever, exceeds that necessary for ionization the distribution of the ions between the gases present will be a function of the ionization potential as well as the stopping power and the partial pressure. For instance, in a $CH_4/2O_2$ mixture a 14.1 volt electron can form O_2^+ ions by direct impact, but CH_4^+ ions can only result from secondary processes when the electron energy is below 15.0 ± .2 volts. The number of CH_4^+ ions formed, therefore, is less than would be expected from the ratio of the two gases present.

In the light of the above consideration, the best that can be done is to see if a reasonable value can be obtained for the ratio of M/N. Assuming that the total expenditure of energy is divided equally between ionizing and non-ionizing processes a ratio of $M/N \doteq 6$ is obtained if the ionizing efficiency for oxygen is three or more times greater than for methane. It seems reasonable that this difference in efficiency should exist for the slow speed electrons found in the positive column. At pressures above 5.5 mm. where ionic chain reactions are in evidence the M/N ratio rises rapidly with increasing pressure.

The Mechanism. It was pointed out in the preceding papers [6],[7] that the ratio of M/N may be a statistical rather than a fixed quantity. Nevertheless, it is interesting to note that in every case so far studied the observed value is either expressed by the simplest equation that can be written for the combining gases, or in the case for water, by the simplest equation multiplied. by two. The combination of CH_4^+ with two molecules of oxygen is the simplest combining ratio for the present reaction; the value of $M/N = 3$ thus obtained is obviously too low. From the results of the decomposition experiments it seems probable that the reaction might be expressed by the following equations:

$$(1)\quad (2CH_4)^+ + O_2 = (C_2H_4)^+ + 2H_2O$$

$$(2)\quad (C_2H_4)^+ + 2O_2 = (2CO_2.2H_2O)^+ \text{ (wall)}$$

This gives a ratio of $M/N = 6$, which is of the order of magnitude of that observed, and is certainly not far from correct.

The equations just presented possess the further advantage of accounting for the character of the deposit on the walls of the tube. It will be recalled that in the case of the oxidation of hydrogen and carbon monoxide, the reaction products were frozen out in sharply defined bands near the cathode, thus indicating a wall neutralization of the ion clusters. In the present case, the banded deposit was still in evidence, showing that wall neutralization was an important factor, but at the same time a deposit was observed well up along the walls of the tube, showing that an appreciable number of neutral molecules were formed in the gas phase. The equations given above permit the formation of two neutral water molecules in the gas phase for every two water and two carbon dioxide molecules neutralized on the walls.

The writers wish to thank Mr. J. W. Westhaver for his assistance in procuring part of the data presented in this paper.

Summary

Methane is converted quantitatively into ethylene and hydrogen in the glow discharge at liquid air temperatures. Approximately one molecule of ethylene is formed per CH_4^+ ion.

The reaction in a $CH_4/2O_2$ mixture goes entirely to carbon dioxide and water. In contrast to a $2H_2/O_2$ mixture no hydrogen peroxide is formed.

The rate of oxidation is accelerated by excess methane; oxygen retards the rate even more than does argon. From this it is concluded that the reaction is initiated primarily by CH_4^+ ions.

The reactivity is most pronounced in the negative glow, is negligible in the dark spaces, and is fairly constant throughout the positive column. The observed ratio of molecules formed to CH_4^+ ions is about seven; probably $M/N \doteq 6$ is nearer the correct value.

The efficiency of the positive column in terms of electron volts per molecule increases rapidly with the pressure above 5.5 mm., indicating the presence of ionic chain reactions.

THE EFFECT OF PREHEATING ON THE DISPERSITY OF CALCIUM CASEINATE IN SKIM MILK*

BY J. B. NICHOLS,[1] E. D. BAILEY,[1] G. E. HOLM,[2] G. R. GREENBANK,[2]
AND E. F. DEYSHER[2]

Casein is suspended in milk in the form of highly dispersed calcium caseinate which may be separated from the serum by means of a clay or collodion ultrafilter or by high-speed centrifuging.[3]

Attempts to estimate the degree of dispersion of calcium caseinate have been made by Svedberg, Wiegner, and Bechhold.[4] Svedberg and Fåhraeus, from preliminary ultracentrifugal studies made in 1924, concluded that the particles were of the order of magnitude of 10 to 70 $m\mu$ radius ($m\mu = 10^{-7}$cm).

Wiegner considers that the major proportion of the particles are amicrons and that the probable range in size is from 5 $m\mu$ to 100 $m\mu$ in diameter. He found the number of particles to be constant even when the milks had been heated or slight amounts of acid had been added. Bechhold considers, from ultrafiltration data on a series of proteins and inorganic colloids, that the calcium caseinate particles in milk are probably greater than 40 $m\mu$ in diameter.

The dispersity of calcium caseinate is of considerable practical as well as theoretical interest. One of the chief problems of the evaporated-milk industry, as well as of other branches of the dairy industry, is the development of proper stability to heat. Little is known concerning the mechanism involved in coagulation, though the industrial methods used for its prevention are well established. In the manufacture of evaporated milk, the milk is first heated to 95°C. for a short time prior to its concentration. This practice insures a greater stability of the finished product in the sterilization process. If temperatures of approximately 70°C. are used, the tendency seems to be to decrease the stability.[5]

These heat treatments also seem to affect certain physical properties of the dispersion. For example, heating milk to 70° lowers the viscosity of the milk, whereas heating to higher temperatures increases the viscosity. These changes in viscosity are accompanied by changes in density (unpublished data). Though stabilization is affected largely by the electrolytes present in the serum, it is possible that the process may depend in part upon changes in particle size. Ultracentrifuge studies were therefore undertaken to determine the distribution curve of untreated calcium caseinate and to ascertain whether heating affects the distribution of particles in skim milk.

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[1] Experimental Station, E. I. du Pont de Nemours & Company.

[2] Bureau of Dairy Industry, U. S. Department of Agriculture.

[3] Friedenthal: Ber., **44**, 904 (1911); Van Slyke and Bosworth: New York (Geneva) Agr. Exp. Sta. Tech. Bull. 39.

[4] Svedberg: Kolloid-Z., **51**, 10 (1930); Wiegner: Z. Nahr. Genussm., **27**, 425 (1914); Bechhold: Z. physik. Chem., **60**, 257 (1907).

[5] Deysher, Webb, and Holm: J. Dairy Sci., **12**, 80 (1929).

Experimental

Preparation of Samples:

Fresh skim milk was warmed to approximately 40°C. and passed through a De Laval clarifier three times in order to remove as completely as possible the finely divided fat, leucocytes, and other material of relatively large particle size. One sample was heated on a water bath at 65°C. and another at 95° for ten minutes in flasks equipped with reflux condensers. These samples, as well as a control sample, were then packed in ice until used in the following experiments. Since the amount of calcium united with casein is a function of the electrolyte content of the serum, serum from the original milk was used as a diluent to maintain the original equilibria throughout the experiments. This serum was obtained by means of a collodion ultra-filter and was kept in ice until used. When a sample was allowed to stand at room temperature for some time a flocculent precipitate formed which presumably was a calcium phosphate.

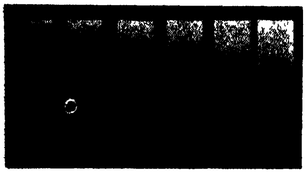

FIG. 1.
Sedimentation of unheated skim milk (Pictures taken at 10-minute intervals)

Ultracentrifugal Determinations:

In the ultracentrifugal determination of the particle-size distribution of a polydisperse material, the following modified form of Stokes' law is used to determine the radius of a particle[1]:

$$r = \sqrt{\frac{9\eta \ln ((x+a)/a)}{2(\rho_p - \rho_l)\,\omega^2 t}}$$

where r is the radius of the particle in centimeters, η the viscosity of the medium, ρ_p the density of the particle, ρ_l the density of the medium, $\omega \left(= 2\pi\frac{N}{60}\right)$ the angular velocity, N the centrifuge speed in r.p.m., t the time of centrifuging in seconds, x the distance in centimeters along the cell from the meniscus, and a the distance of the meniscus from the center of rotation. The other data needed in addition to that obtained from the ultracentrifuge for the determination of the distribution curve are the viscosities of the solutions, the density of the calcium caseinate particles, and the density of the serum in which the particles are dispersed. Table I gives these data.

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[1] For the theory underlying the determination of distribution curves by means of the ultracentrifuge, see Svedberg and Rinde: J. Am. Chem. Soc., **46**, 2681-2685 (1924); Rinde: "The Distribution of the Sizes of Particles in Gold Sols," Diss. Upsala, 1928; and Svedberg: "Colloid Chemistry," Second Edition, pp. 171 et seq. (1928).

The apparent density of the calcium caseinate was taken as the reciprocal of the partial specific volume. In order to calculate the partial specific volume from the pycnometric data, the concentration of the suspended solids, composed mainly of calcium caseinate, must be determined accurately.

Skim milks are quite constant in the amount of lactalbumin and lactoglobulin they contain, this value being approximately 0.55%.[1] The serum used contained 0.40% of protein, hence a portion of the soluble proteins was retained by the filter. Had no lactalbumin or globulin been retained by the filter the protein content of the serum would have been approximately 0.55% and the resulting solids content approximately 6.37%. Thus 3.03% (=9.40 − 6.37) of the solids of skim milk represents the content of suspended solids, mainly calcium caseinate. In addition to calcium caseinate the fraction undoubtedly contains a small amount of highly dispersed fat, some leucocytes, and perhaps some colloidal phosphates.

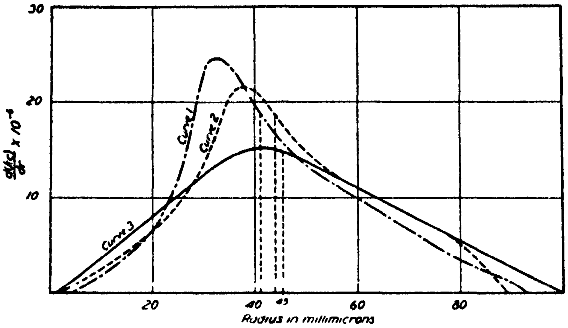

FIG. 2.

"Weight optical" distribution curves of calcium caseinate from milk

(1) Heated to 95°C.
(2) Heated to 65°C.
(3) Unheated

Curve areas
Curve 1-87%
Curve 2-85%
Curve 3-81%

1 sq. = 20%

TABLE I

	Skim Milk	Serum
Solids*	9.40%	6.22%
Proteins	3.39%	0.40%
Density at 30°C.	1.0317	1.022

Apparent density of calcium caseinate = 1.504
Viscosity of serum at 30°C. = 0.0116
Viscosity of 4:1 serum-skim milk at 30°C. = 0.0120

* Solids content determined at 100°C and 25-27 in. vacuum.

From other data on these samples the weight of the calcium caseinate has been calculated as 2.94%. From these considerations and for the purpose at hand 3.03% has been chosen as the total amount of the suspended phase. The value found for V, the partial specific volume, was 0.665, or 1.504 for the apparent density of the calcium caseinate.

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[1] Rogers: "Fundamentals of Dairy Science," p. 43 (1928).

The three samples of skim milk ((1) control, (2) sample heated to 65°C. for ten minutes, and (3) sample heated to 95° for ten minutes), which contained approximately 3% of solids, were diluted to one-fifth the original concentration with the milk serum prepared by ultrafiltration and centrifuged at a speed of 4,000 r.p.m. Eastman Process Plates were used to record the effect of centrifuging. Since the illumination came from a Pointolite lamp, the effective radiation was the blue region of the spectrum. Exposures ten and fifteen seconds in length were made every ten minutes, each exposure yielding data on which a complete distribution could be calculated. Figure 1 represents a series of photographic exposures taken of the sedimenting calcium caseinate in the control sample. The exposure at the left represents the sedimentation which has occurred in the first ten minutes, and the succeeding exposures represent the condition at ten-minute intervals up to sixty minutes from the start. The weight-optical distribution curves obtained for the three samples are shown in Fig. 2. The three distribution curves are similar enough to be considered almost identical within the limit of experimental error, although there is an indication of a slight shift in the mean radius to a smaller particle size as the temperature of forewarming is raised —from a mean size of 45mμ for the control sample to a mean size of 41 mμ for the sample heated to 95°C. This slight shift could hardly account for the rather large differences in stability observed for the samples when subjected to the coagulation test subsequent to forewarming.

Discussion

The results indicate that the calcium caseinate particles in milk range in size from about 100 mμ radius (200 mμ diameter) down to molecular sizes, which, according to recent work of Svedberg, Carpenter, and Carpenter[1] are of the order of 4 mμ radius for casein. The mean radius is 40 to 50 mμ (80 to 90 mμ diameter). However, an appreciable portion (ca. 15% on the basis of its light absorption) of the suspended material had left the field of observation between the time of the original exposure of the photographic plate and the second exposure ten minutes later. This fraction undoubtedly consists of small amounts of fat, leucocytes, some colloidal calcium phosphate and perhaps some large aggregates of calcium caseinate.

In a polydisperse system having the range of sizes of the calcium caseinate system under consideration, the light absorption of particles increases rapidly with increasing radius in accordance with the Rayleigh scattering of small particles; therefore, the curves presented in Fig. 2 do not represent the true relation of weight of material to radius but the so-called weight-optical relation, the term "weight-optical" referring to an apparent concentration which is the product of the absorption constant k of the given radius by the concentration c of material of that radius. If the distribution curves had been markedly different this variation of light absorption with particle size would have rendered difficult the comparison of the different samples. However, since the curves are so nearly identical in spite of the large variation of light absorption with particle size, we may safely conclude that the particle-size distribution of calcium caseinate is very little affected by forewarming up to 95°C. for a short time.

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[1] Svedberg, Carpenter, and Carpenter: J. Am. Chem. Soc., **52**, 241, 701 (1930).

Prolonged heating of milk results in flocculation; thus it would be entirely reasonable to suppose that the particles would increase progressively in size with the time and temperature of heating.[1] Although this may occur in the later stages, the results presented indicate that particle-size changes are not of primary importance in the phenomenon of the stabilization of a milk to heat by forewarming, that is, unless the *ad hoc* assumption is made that the small shifts in the distribution curve to smaller particle sizes are capable of producing the large changes in stability observed. Hydrolytic changes may be responsible for the stabilization.

Summary

1. The weight-optical particle-size distribution curves have been determined for samples of the calcium caseinate of skim milk subjected to different temperatures of preheating.
2. The majority of the material is less than 200 mμ in diameter with a mean size of about 90 mμ.
3. A small amount of coarser material, probably colloidal calcium phosphate and large aggregates of calcium caseinate, is also present.
4. Preheating up to 95°C. has little effect on the distribution curve of particle size.

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[1] Svedberg, Carpenter, and Carpenter: loc. cit. p. 708, have observed an increase in size of the casein molecule at 40°C; if such a low-temperature change occurs in the calcium caseinate suspension in skim milk, the control sample would undergo the same change as the heated samples because the milk was warmed to 40°C. previous to skimming.

THE ADSORPTION OF WATER FROM ETHYL ALCOHOL-WATER MIXTURES BY SILICA GEL*

BY HENRY MAUZEE DAVIS AND LLOYD E. SWEARINGEN

Introduction

The problem of producing ethyl alcohol of more than 94 to 95% purity from mixtures of the alcohol and water has been the object of many investigations. The problem reduces almost entirely to one of devising a method for breaking up or changing the composition of the azeotrope formed by these two substances.

Both chemical and physical methods have been used to accomplish this result. Of the chemical procedures for removing water from alcohol-water mixtures, distillation from quick lime or sodium are the most common. The nearness of the constant boiling temperature of the azeotrope to the boiling point of pure alcohol makes ordinary fractional distillation impractical. Young and Fortey,[1] by adding benzene to the alcohol-water azeotrope converted it into a lower boiling point ternary system. Alcohol of high purity is recoverable from this ternary system on distillation. Wade and Merriman,[2] making use of the fact that the composition of the azeotrope is influenced by pressure, have succeeded in producing alcohol of high purity by fractional distillation under reduced pressure. Thus, starting with an alcohol-water mixture containing 5.14% water, after ten fractionations under pressures of 57-59 mm. mercury, only 0.95% water remained. Grimm and Wolff,[3] and Grimm, Raudenbusch and Wolff[4] have successfully broken up azeotropic mixtures of ethyl alcohol and carbon tetrachloride by adsorption processes, using silica gel as the adsorbent.

Since it has been demonstrated that the composition of an azeotropic mixture can be changed by the preferential adsorption of one component of the mixture, this procedure should yield results with the alcohol-water system. Since silica gel is know to have a high adsorptive capacity for water, it should be a good medium for the removal of water from the alcohol-water mixtures.

The adsorption of fluids by silica gel is generally conceded to be a process of capillary condensation.[5] Within the minute capillaries of this adsorbent, the surface of any condensed liquid must have a radius of curvature about equal to that of the capillary in which it stands. The vapor pressure of a liquid in a capillary tube is lower than the vapor pressure of the liquid over the plane surface. The Kelvin equation, $\ln \frac{P}{P_0} = -\frac{2\sigma v}{RTr}$ affords a means of predicting the magnitude of the vapor pressure lowering in small capillaries. P_0 and P are the vapor pressures over the plane and concave surfaces respectively, at temperature T, R is the gas constant, σ the surface tension, r the radius of the capillary and v the molar volume of the liquid. Shereshefsky[1] has shown that the vapor pressure lowering for water in small capillaries is much greater than can be accounted for by the Kelvin equation. His results indicate that this lowering of the vapor pressure is due to the increase in surface tension of the water.

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* Contribution from the Chemical Laboratory, University of Oklahoma.

[1] J. Chem. Soc., 81, 717, 739 (1902).

[2] J. Chem. Soc., 99, 997 (1911).

[3] Z. angew. Chem., 41, 98 (1928).

[4] Z. angew. Chem., 41, 104 (1928).

[5] Patrick and Eberman: J. Phys. Chem., 29, 220 (1925).

The Kelvin equation predicts that the greater the surface tension of the liquid, the greater will be the reduction in vapor pressure. That is, P/P_0 is proportional to $e^{-\sigma}$. The surface tension of water will vary from three to four times greater than that of ethyl alcohol between 0°C. and the boiling point of alcohol. The molar volumes of water and alcohol, near the boiling point of alcohol will be roughly in the ratio of 18 to 63. The radius of the capillaries being the same for both water and alcohol, then the lowering of the vapor pressures for each of these liquids should be proportional to their respective $(\sigma v/T)$ values. It is seen that the $(\sigma v/T)$ value for water is slightly greater than the $(\sigma v/T)$ for alcohol. Consequently the vapor pressure lowering for water in the capillaries of silica gel should be greater than the vapor pressure lowering for alcohol. It follows that the component suffering the greatest vapor pressure lowering will be more readily condensed.

The preferential adsorption of water from an alcohol-water mixture, which this treatment predicts, is somewhat meager. It is further complicated by the fact that the heats of wetting of silica gel by alcohol and water are slightly different. Grimm, Raudenbusch and Wolff[2] report the heats of wetting of silica gel by alcohol and water to be 23.7 and 20.95 calories per gram, respectively. However, it was believed that if the proper conditions could be discovered, the passage of vapor from the alcohol-water mixture over silica gel should result in the adsorption and removal of at least a part of the water vapor from the mixture. Subsequent condensation of the vapor phase remaining should yield an alcohol-water mixture enriched in alcohol.

Experimental

The general plan for attacking the problem may be stated in the following manner. The vapors from the boiling alcohol-water mixture were passed through a column of silica gel, maintained at some suitable temperature above the boiling point of alcohol and below the boiling point of water. The surviving vapors were then condensed and collected in 10 c.c. portions. The composition of each of these portions was determined by specific gravity methods. Fifty cubic centimeters of the alcohol-water mixture were used in each experiment. Fifty-six grams of silica gel, prepared by Patrick's method, were used in each experiment, except as otherwise noted. The silica gel was packed loosely in a straight piece of glass tubing, 45 cm. long and 2 cm. in diameter. The gel column was kept at the desired temperature by means of a water bath. The gel was activated by heating to 130°C. under a pressure of from 25-28 mm. of mercury.

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[1] J. Am. Chem. Soc., 50, 2966 (1928).

[2] Loc. cit.

The Effect of Temperature on the Adsorption Process.

The effect of temperature on the adsorption process is complicated somewhat by the fact that considerable quantities of heat are evolved during the adsorption process. The data in Table I show that the temperature of the adsorbent may vary from 2° to 15°C. above the temperature of the constant temperature bath. These experiments were carried out with a thermometer imbedded in the gel column, about midway of the column. The temperature of the gel column and that of the constant temperature bath were compared several times during the distillation of an alcohol-water sample. These experiments were made on an alcohol-water mixture containing 7.4% water. A typical set of data are given in Table. I

TABLE I

The Variation in the Temperature of the Adsorbent due to Heat of Wetting.

Time of Reading	Temperature of Bath	Temperature of Adsorbent	Remarks
3:55 P.M.	82°C.	82°C.	Vapors enter gel column.
——	81.8°	96°	Vapors emerge from gel column.
3:58	82.0°	97°	
4:01	81.7°	90°	
4:06	82.0°	85°	
4:09	82.0°	84.5°	
.	.	.	Temperature of adsorbent never below 84°C.
4:18	82.0°	84.0°	
.			

Table II and Fig. 1 give the results of experiments carried out for the purpose of determining the optimum temperature for water removal from a given alcohol-water mixture. The samples used in these experiments contained 7.4% water, weight percent. All conditions except temperature were maintained uniform throughout these experiments.

From Table I it is seen that the heat of wetting is sufficient to keep the gel at least 2°C. above the temperature of the bath as long as vapors are passing through. In experiments number 8 to 12, Table II, the bath temperature was kept below the boiling temperature of the mixture, with the expectation that the heat of wetting would keep both components largely in the vapor phase. However, due to the fact that the walls of the tube containing the gel remained at the temperature of the bath, a considerable amount of purely thermal condensation occurred. This condensate was trapped in

TABLE II

The Effect of Temperature of the Adsorbent on Water Removal

Experiment Number	Bath Temperature	Best Fraction	Maximum Percent Water lost	Percent of Total Sample retained by Gel.
1.	91.5°C.	2	0.76	16
2.	86.5	1	1.12	16.2
3.	84.6	2	1.14	22.8
4.	83.5	2	1.44	24.8
5.	82.0	1	1.76	....
6.	80.0	1	2.39	25.8
7.	78.0	1	2.71	24.0
8.	77.2	1	2.20	34.4
9.	76.5	1	2.17	41.0
10.	75.4	1	2.31	48.8
11.	74.5	1	2.62	54.0
12.	72.0	1	2.62	66.0

the gel column. Data given in Table II show how important purely thermal condensation becomes at temperatures below 78°C. Table II makes the meaning of Fig. 1 rather apparent. At temperatures well below the boiling point of the mixture, (Ex. No. 11 and 12) the percent of water lost (in the liquid phase) is approximately constant. As we approach the boiling point of the mixture, (Ex. No. 10, 9 and 8) while we have increasingly larger quantities of vapor phase present, the liquid present apparently effectively prevents it from being adsorbed to any appreciable extent. Once the boiling point of the mixture is passed, the amount of water adsorbed increases rapidly to a maximum, just above the boiling point of pure alcohol. When considerable quantities of both liquid and vapor phases are in contact with the gel, the amount of water removed is smaller than for either of the phases present in large excess. The amount of water removed again falls off as the boiling point of water is approached. The results indicate that the removal of water from the alcohol mixtures is more pronounced in the vapor than in the liquid phase. The optimum bath temperature for water removal is 78°C.

The Effect of Water Content of Mixtures on the Amount of Water adsorbed from Alcohol-Water Mixtures.

Data for other alcohol-water mixtures, including the true azeotrope are given in Table III and Fig. 2. These data were obtained in experiments similar to those used for the data in Table II, except that all conditions except composition were maintained constant. The composition of the true azeotrope for the particular pressure desired (737.4 mm.) was obtained by interpolation of the data of Wade and Merriman. It contained 95.62% alcohol and boiled with utter constancy at 77.26°C. The gel column was maintained at 78° to 78.2°C.

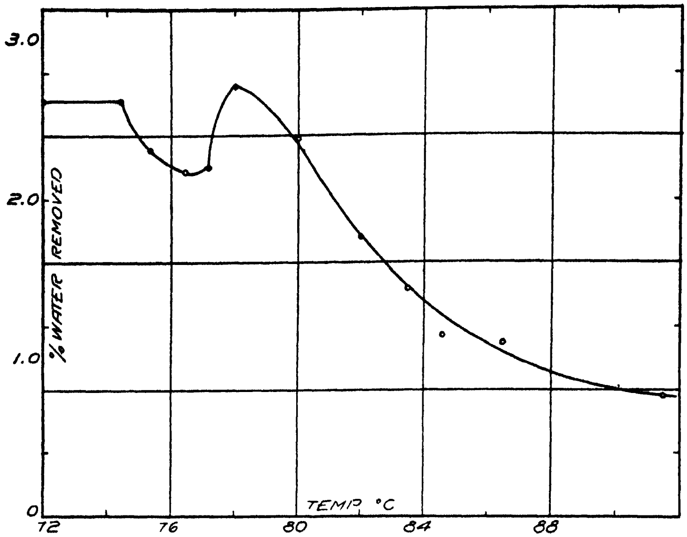
3.0
2.0
1.0
0
% WATER REMOVED
TEMP °C
72
76
80
84
88

Fig 1

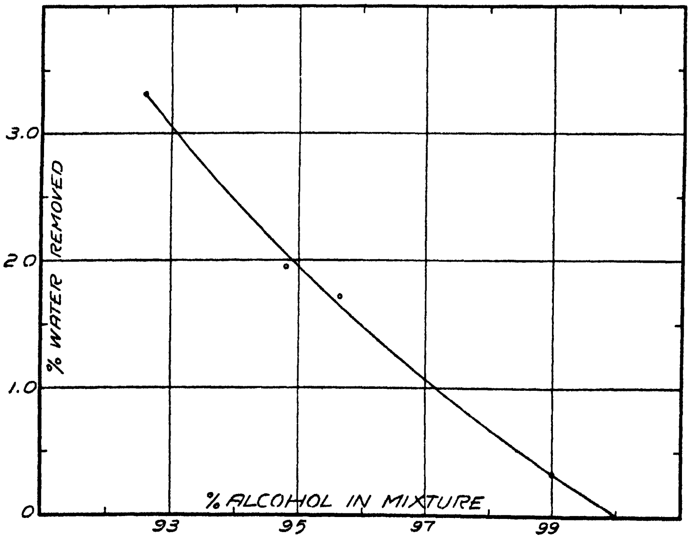
3.0
2 0
1.0
0
% WATER REMOVED
% ALCOHOL IN MIXTURE
93
95
97
99

Fig. 2

TABLE III

The Relation of Water Content of Mixture to Water adsorbed.

Weight Percent Alcohol in Mixture	Percent Water Lost
92.6	3.31
94.8	1.95
95.62+	1.72
99.0	0.33

+ True Azeotrope.

Change in Composition of Condensate during Progress of Distillation.

The results given in Table IV show how the composition of the condensate changed during the progress of a single distillation. Fifty cubic centimeters of the true azeotrope were distilled over 155 grams of gel, the gel temperature being maintained at 78°C. The successive 10 c.c. portions collected showed the following compositions.

TABLE IV

The Relation of Alcohol Content to Fraction collected.

Fraction Number	Alcohol Content	Water Removed
1.	99.11%	3.49%
2.	97.82%	2.20%
3.	96.89%	1.27%
4.	96.25%	0.63%

Effect of Variation in Quantity of Gel.

Experiments similar to those recorded in Table II were carried out with 155 grams of gel, all other factors being maintianed the same. The maximum amount of water lost with this larger quantity of gel was 3.44% as compared with 1.72%. The azeotropic mixture, with 95.62% alcohol was used in these experiments. With 2.76 times more gel present, the water removed is exactly twice as great.

Summary

1. Water may be preferentially adsorbed from alcohol-water mixtures by silica gel.

2. Adsorption of water from the mixtures is greater when adsorption takes place from the vapor than from the liquid phase.

3. The optimum temperature for the preferential adsorption of water vapor from the mixtures has been found to be 78°C.

4. The fraction of the total water present which is removed by adsorption decreases as the total water content of the mixture decreases.

5. The true azeotrope was studied and one fraction of the condensate (about 20% of the quantity started with) recovered showed an alcohol content better than 99%.

6. The adsorption of water increases with an increase in quantity of adsorbent, but not as a direct proportion.

THE SYSTEM NORMAL BUTYL ALCOHOL-METHYL ALCOHOL-WATER

BY A. J. MUELLER, L. I. PUGSLEY AND J. B. FERGUSON

Methyl alcohol is completely miscible in water and in n. butyl alcohol but water and n. butyl alcohol are themselves only partially miscible at ordinary temperatures. The ternary system composed of these liquids does not appear to have been previously investigated. Our results[1] include the values for the binodal curves, the tie lines and the plait points at a series of temperatures ranging from 0°C. to 105°C.

Normal Butyl Alcohol. A carefully prepared product obtained from the British Acetone Company in 1917. After treating with lime in the cold and distillation, it yielded an alcohol with $D_4^{20} = 0.8095$ and boiling point 117.6°C. This density agrees with that given by Reilly and Ralph[2] for the pure alcohol and therefore we assumed the impurity to be water. Pugsley's stock sample was estimated[3] to be 97.25 weight percent alcohol and this he checked by a density determination using a synthetic solution prepared from his dried alcohol and distilled water. Mueller's stock sample was estimated to contain 97.5 weight percent alcohol and on drying he obtained a product with density $D_4^{20} = 0.8097$.

Methyl Alcohol. Eastman Kodak Research Laboratory and Kahlbaum, acetone free. Pugsley's sample gave $D_4^{20} = 0.7938$ and Mueller's gave $D_4^{20} = 0.7923$. Upon the assumption that the impurity was water, the former sample was estimated[4] to contain 99.35 weight percent alcohol and the latter 99.8 percent.

We considered that the water content of the experimental charges would be more accurately known by making an allowance for the water present in the stock alcohols than by working with the absolutely dry alcohols which would so readily absorb moisture from the air. Distilled water was used.

Apparatus and Procedure

For the measurements at 0°C. a glass thermostat containing ice and water was employed. For higher temperatures the bath contained either water or a strong solution of glycerol. The temperature could be regulated to 0.1°C. and the thermometer read to 0.05°C.

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[1] Results at 0°C. by Mr. Pugsley (1927-28), those at other temperatures by Mr. Mueller (1928-29-30).

[2] Reilly and Ralph: Sci. Proc. Roy. Dublin Soc., **15**, 597 (1919).

[3] Young: "Distillation Principles and Processes," 262 (1922).

[4] International Critical Tables, **3**, 116 (1928).

The binodal curves were determined by three methods. At 0°C. Pugsley added a suitable component to a known homogeneous solution of the other components and found, by weighing, the amount of this component necessary to give rise to heterogeneity. At 15°C., 30°C., 45°C. and 60°C. Mueller determined in a similar manner the amount of the consolute (methyl alcohol) required to change a heterogeneous system into a homogeneous one. At higher temperatures, the evaporation losses rendered unsuitable this procedure and a method similar to that of Drouilon[5] was employed. Samples containing equal percentages of methyl alcohol, but different percentages of butyl alcohol and water, were placed in tubes of soda-glass and the tubes sealed, care being taken to leave an air bubble large enough to ensure the presence of a gas phase at all temperatures and to provide adequate stirring. A tube was placed in the thermostat in an inclined position and slowly rotated (46 times per minute) while the bath was either heated or cooled. The critical solution temperature for each sample was thus obtained. Such temperatures were plotted against the n. butyl alcohol-water, content of the samples. A number of such graphs were thus obtained, each graph relating to systems of constant methyl alcohol content. From these graphs, the points on the binodal curves could be obtained.

In the experiments at 15°C.-60°C., a sample was held in a calibrated Pyrex glass tube and the volume of the final homogeneous solution was obtained from cathetometer readings. The densities of these solutions were calculated from the volumes and weights. The volumes of the two phases present in the sample selected for the determination of a tie line were found in a similar manner and the tie lines were then obtained by the graphical method of Miller and McPherson.[6] The tie lines at 0°C. were more directly determined since the two phases were separated, weighed and the weights checked against the original total weight. This rendered unnecessary the approximations involving the densities but the whole procedure was more tedious than the former method.

At 75°C. and 90°C. density determinations were not made and a modification of the latter method was employed. Owing to the high temperatures, certain precautions were necessary since appreciable losses would occur if the sample were exposed to the air even for a short time. A capillary tube was sealed to the bottom of the sample tube and bent so that its upper end was well above the bath liquid. To this end was sealed a stopcock. At 75°C. the phases were separated by forcing the lower layer out through the capillary using compressed air; at 90°C., the vapour pressure alone was sufficient for this purpose, and in this case the upper end of the sample tube was sealed off after filling. The weight of the phase removed was obtained by difference from the weights of the original charge and of the residual layer since the evaporation of the lower layer during its removal rendered the directly determined weight of this phase of dubious value.

[5] Drouilon: J. Chim. phys., **22**, 149 (1925).

[6] Miller and McPherson: J. Phys. Chem., **12**, 709 (1908).

The plait points at 0°C.-75°C. were obtained graphically by drawing a smooth curve through the bisectors of the tie lines to meet the binodal curves. Solutions with compositions corresponding to the location of these points of contact were then made up. To each solution of five cubic centimeters was added two drops of water and the ratio of the volumes of the phases which formed was noted. Three drops of butyl alcohol and sufficient methyl alcohol (usually three drops) to bring the system to such a state that one more drop would cause homogeneity, were added and the ratio of the volumes of the phases which separated was again noted. In the first case, the volume of the aqueous phase was the greater and in the second case the volume of the alcoholic phase was the greater, the excess in each case not exceeding 0.2 cc. The positions of these plait points were checked and established in this manner.

The plait points at 90° and 105°C. were obtained by interpolation from the smooth curve on a ternary diagram connecting our experimental points with the point representing the consolute composition in the binary system.

Sources of Error

Measurements at 0°C. to 60°C. The temperature of the thermostat was held to within 0.1°C. and the actual temperatures were accurate within these limits.

The sample tube was kept stoppered as much as possible during a determination. The time, exclusive of time taken for weighings, required to establish a point on the binodal curve seldom exceeded an hour. A test with methyl alcohol, the most volatile component, indicated that the loss by evaporation at 50°C. in one hour was 0.0135 g. A loss of this amount would correspond to an error of 0.17 weight percent in the total composition.

Upon the assumption that the solution-air surface was elliptical, a volume reading of 3 cc. was in error not more than 0.3 weight percent.

The detection of homogeneity or heterogeneity was not difficult but the composition of the saturated solution could only be determined to one drop of the liquid which was added. Care was taken to use as small drops as possible and the error was not greater than 0.11 weight percent of the composition of the system.

The liquid-liquid interface was plainly visible, and the cathetometer reading readily obtained.

Measurements above 60°C. Owing to the uncertainty in the stem correction of our mercury thermometer, the accuracy of the temperature measurements was 0.2°C. at 100°C. and 0.3°C. at 120°C.

The temperature difference between the thermometer bulb and the liquid in the sample tube was probably not in excess of 0.1°C. except at the highest temperatures. The change from heterogeneity to homogeneity and vice versa could be determined for points on the flat parts of the temperature-composition curves within a range of 0.2°C. but toward the ends of these curves only to within 0.8°C. An error of not more than 0.5 percent in the butyl alcohol or water content (B + W = 100) might be caused through this source.

In any one series of experiments, the methyl alcohol was maintained as nearly constant as possible. The actual deviations from constancy are indicated in the table of results. This degree of constancy was deemed sufficient in view of the other sources of error but to attain even this degree, with the small samples (4-6 g.) used, it was necessary to discard one in every four samples prepared (approx.) at a time when we were experienced in the art.

Jones[7] reports a difference between results obtained using soda glass and Pyrex glass when studying the system water-n. butyl alcohol. Since our experiments were made with containers of soda glass, we repeated this comparison and observed with fresh soda glass a consolute temperature 0.4°C. higher than that observed with Pyrex glass. Jones' observation was thus confirmed. If the results with Pyrex glass are the more accurate, then our results are subject to this error, the magnitude of which would vary from experiment to experiment, especially with experiments at different temperatures and which would probably have a maximum value of 0.4°C. Since most of our experiments were made at temperatures much lower than the consolute temperature in the binary system, we did not consider that the possible magnitude of this error warranted a repetition of the many measurements which we had previously obtained.

Weighings were made to 0.0001 g. using carefully standardized weights but owing to the nature of our results, the weights recorded in this paper have usually been rounded off to three significant figures.

Experimental Results and Discussion

In the tables the following abbreviations are used: n. butyl alcohol, B, methyl alcohol, M; water, W. The results have been calculated on the basis B + W = 100, since the infinite diagram enables one to select a scale suitable for the indication of the methyl alcohol content.

Tables I to V, inclusive, give our results at 0°C., 15°C., 30°C., 45°C., and 60°C. In Table VI are tabulated the critical temperatures observed with the various series of samples, each series at constant methyl alcohol content. The results on the binodal curves at 75°C., 90°C., and 105°C. are given in Table VII, and those on the tie lines at 75°C. and 90°C. in Table VIII. The composition of the plait points at various temperatures are given in Table IX. The temperatures of a series of points on the saturation surface (solid model) corresponding to systems of constant butyl alcohol and water contents but variable methyl alcohol content are given in Table X.

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[7] Jones: J. Chem. Soc., **1929**, 799.

TABLE I

Binodal Curve, Tie Lines and Plait Point at 0°C.

Binodal Curve

Composition in grams			Composition in grams		
M.	W.	B.	M.	W.	B.
—	90.45	9.55*	16.87	56.76	43.24
2.89	90.21	9.79	15.70	46.77	53.23
4.68	90.07	9.93	14.34	44.52	55.48
9.68	89.26	10.74	12.38	37.20	62.80
13.03	86.72	13.28	9.80	32.33	67.67
16.73	83.63	16.37	6.47	25.86	74.14
19.03	76.70	23.30	3.518	22.91	77.09
18.52	66.55	33.45	—	19.62	80.38*

* H. & M. extrapolated.

Tie Lines

	Comp. of system			Phase weight ratio
	M.	W.	B.	
(a)	5.81	62.46	37.54	0.697
(b)	10.69	60.68	39.32	0.870
(c)	14.30	63.18	36.82	0.840
(d)	16.72	64.60	35.40	0.702
(e)	17.62	63.31	36.69	0.941

	Comp. upper phase			Comp. lower phase		
	M.	W.	B.	M.	W.	B.
(a)	4.20	23.30	76.70	7.00	90.00	10.00
(b)	8.75	30.10	79.90	12.50	87.50	12.50
(c)	12.25	36.90	63.10	15.50	84.80	15.20
(d)	14.50	44.25	57.20	18.90	79.50	20.50
(e)	16.50	51.50	48.50	19.40	74.50	26.50

Plait Point 18.50 M. 63.10 W. 36.90 B.

TABLE II

Binodal Curve, Tie Lines, Plait Point and Density Determinations at 15°C.

Binodal Curve

Comp. in grams			Density	Comp. in grams			Density
M.	W.	B.		M.	W.	B.	
				16.0	66.1	33.9	0.926
—	91.7	8.30*	0.988	15.7	61.1	38.9	0.922
6.29	91.4	8.56	0.981	15.1	54.5	45.5	0.913
12.2	89.3	10.7	0.981	14.6	48.7	51.3	0.899
14.4	86.8	13.2	0.970	13.3	42.8	57.2	0.890
15.7	83.9	16.1	0.960	11.1	36.2	63.8	0.881
16.2	80.5	19.5	0.954	7.63	29.0	71.0	0.870
16.7	76.0	24.0	0.945	2.55	21.9	78.1	0.861
16.3	71.3	28.7	0.934	—	19.9	80.2*	0.853

* (H. & M. interpolated).

Tie Lines

	Comp of system			Phase volume ratio	Phase weight ratio
	M.	W.	B.		
(a)	3.64	61.1	38.9	1.13	1.29
(b)	6.55	61.1	38.9	1.11	1.25
(c)	8.90	61.1	38.9	1.05	1.18
(d)	11.4	61.1	38.9	0.965	1.07
(e)	14.1	61.1	38.9	0.830	0.900
(f)	15.3	64.2	35.8	0.975	1.06

	Comp. upper phase			Comp. lower phase		
	M.	W.	B.	M.	W.	B.
(a)	2.3	21.7	78.3	4.8	91.6	8.4
(b)	4.3	24.0	76.0	8.4	90.7	9.3
(c)	6.7	27.5	72.5	10.7	89.7	10.3
(d)	9.3	32.4	67.6	13.2	88.0	12.0
(e)	12.7	40.5	59.5	15.6	83.9	16.1
(f)	14.4	47.8	52.2	16.3	80.0	20.0

Plait Point 16.0 M. 64.5 W. 35.5 B.

TABLE III

Binodal Curve, Tie Lines, Plait Point and Density Determinations at 30°C.

Binodal Curve

Comp. in grams			Density	Comp. in grams			Density
M.	W.	B.		M.	W.	B.	
—	92.92	7.08*	0.985	14.3	75.9	24.1	
4.71	92.3	7.67		14.2	73.1	26.9	
6.12	92.1	7.94	0.975	14.2	71.8	28.2	0.928
7.55	91.1	8.87	0.961	13.9	67.3	32.7	0.918
8.23	90.8	9.17		13.8	61.9	38.1	0.911
9.08	90.7	9.34	0.979	13.4	57.2	42.8	0.904
11.06	89.1	10.91	0.971	11.2	48.0	52.0	0.888
12.3	87.1	12.9	0.958	11.0	44.4	55.6	0.881
13.5	83.6	16.4	0.953	9.50	39.0	61.0	0.874
14.1	82.0	18.0		8.21	35.2	64.8	0.870
13.9	80.6	19.4	0.946	6.54	31.0	69.0	0.863
14.3	79.0	21.0		3.97	26.1	73.9	0.854
14.2	76.1	23.9	0.938	—	20.6	79.4*	0.842

* H. & M.

Tie Lines

	Comp. of system			Phase volume ratio	Phase weight ratio
	M.	W.	B.		
(a)	3.98	71.0	29.0	1.93	2.20
(b)	7.95	71.0	29.0	1.93	2.15
(c)	9.83	68.5	31.5	1.62	1.78
(d)	11.1	68.5	31.5	1.64	1.78
(e)	12.3	68.5	31.5	1.64	1.77
(f)	13.6	68.5	31.5	1.78	1.88

	Comp. upper phase			Comp. lower phase		
	M.	W.	B.	M.	W.	B.
(a)	2.4	23.8	76.2	4.7	92.4	7.6
(b)	5.3	28.4	71.6	9.1	90.7	9.3
(c)	7.5	33.0	67.0	11.2	88.8	11.2
(d)	8.5	35.9	64.1	12.5	86.7	13.3
(e)	10.0	41.5	58.5	13.5	83.8	16.2
(f)	12.3	52.2	47.8	14.2	77.2	22.8

Plait Point 13.9 M. 65.5 W. 34.5 B.

TABLE IV

Binodal Curve, Tie Lines, Plait Point and Density Determinations at 45°C

Binodal Curve

Comp in grams			Density	Comp. in grams			Density
M.	W.	B.		M.	W.	B.	
—	93.5	6.50*	0.982	11.7	60.8	39.2	0.905
.789	93.82	6.18	0.982	10.8	54.4	45.6	0.900
3.89	93.1	6.87	0.978	10.5	51.1	48.9	0.898
8.14	90.3	9.67	0.963	10.1	47.4	52.6	0.895
9.87	87.3	12.7	0.961	9.16	42.9	57.1	0.885
10.7	84.2	15.8	0.949	9.20	40.8	59.2	0.864
11.1	81.3	18.7	0.942	7.94	36.1	63.9	0.859
11.3	78.6	21.4	0.935	5.77	30.7	69.3	0.851
12.0	75.8	24.2	0.930	2.40	24.4	75.6	0.837
11.9	71.8	28.2	0.925	—	21.8	78.2*	0.833
11.8	67.4	32.6	0.918				

* (H. & M. interpolated).

Tie Lines

	Comp. of system			Phase volume ratio	Phase weight ratio
	M.	W.	B.		
(a)	3.10	60.8	39.2	0.930	1.08
(b)	6.25	60.8	39.2	0.850	0.963
(c)	8.25	60.8	39.2	0.768	0.865
(d)	9.86	60.8	39.2	0.670	0.758
(e)	11.0	66.2	33.8	1.00	0.964

	Comp. upper phase			Comp. lower phase		
	M.	W.	B.	M.	W.	B.
(a)	3.4	25.9	74.1	2.7	93.3	6.7
(b)	5.9	30.9	69.1	6.3	91.8	8.2
(c)	7.8	36.1	63.9	8.5	89.5	10.5
(d)	9.3	43.0	57.0	10.5	85.0	15.0
(e)	10.7	52.7	47.3	11.5	79.0	21.0

Plait Point 11.5 M. 66.0 W. 34.0 B.

TABLE V

Binodal Curve, Tie Lines, Plait Point and Density Determinations at 60°C.

Binodal Curve

Comp. in grams			Density	Comp. in grams			Density
M.	W.	B.		M.	W.	B.	
—	93.5	6.52*	0.977	9.64	61.0	39.0	0.877
5.54	90.89	9.11	0.962	8.55	52.8	47.2	0.875
6.12	90.3	9.67	0.960	8.13	45.4	54.6	0.858
6.42	90.2	9.80	0.957	6.78	39.0	61.0	0.847
8.59	86.4	13.6	0.940	4.44	32.0	68.0	0.836
9.05	82.4	17.6	0.936	2.49	28.1	71.9	0.830
9.93	73.7	26.3	0.921	—	23.6	76.4*	0.825
9.80	68.7	31.3	0.894				

* H. & M.

Tie Lines

	Comp. of system			Phase volume ratio	Phase weight ratio
	M.	W.	B.		
(a)	5.36	66.9	33.1	1.32	1.53
(b)	7.41	66.8	33.2	1.22	1.36
(c)	8.37	66.8	33.2	1.18	1.29
(d)	1.91	67.0	33.0	1.34	1.57

	Comp. upper phase			Comp. lower phase		
	M.	W.	B.	M.	W.	B.
(a)	1.5	26.3	73.7	2.2	92.8	7.2
(b)	4.1	31.3	68.7	6.2	90.3	9.7
(c)	6.5	38.3	61.7	8.0	87.7	12.3
(d)	7.7	43.3	56.7	8.8	85.2	14.8

Plait Point 9.71 M. 66.8 W. 33.2 B.

TABLE VI

The Critical Temperatures of Various Series of Systems, Each at Constant Methyl Alcohol Content

Methyl Alcohol M = 2.0 when B + W = 100

Composition of system			Critical Temperature °C.	% dev. of M. from series unit	Average range of critical temperature °C.
M.	W.	B.			
.105	4.60	.398	82.0	4.4	0.1
.102	4.51	.503	95.6	1.2	0.2
.102	4.42	.587	101.7	1.7	0.4
.101	4.21	.804	109.4	0.3	0.1
.103	3.71	1.29	113.2	3.2	0.2
.102	3.03	1.97	113.3	1.4	0.1
.0885	2.08	2.42	107.2	1.6	0.8
.0709	1.36	2.15	96.8	1.2	0.7
.0700	1.14	2.37	82.2	0.2	0.2

TABLE VI (continued)

Methyl Alcohol M = 2.5 when B + W = 100

Composition of system			Critical Temperature °C.	% dev. of M. from series unit	Average range of critical temperature °C.
M.	W.	B.			
.128	4.20	.800	105.8	2.3	0.2
.126	3.78	1.24	109.9	0.6	0.1
.099	2.60	1.40	110.4	0.9	0.3
.100	2.17	1.83	108.7	0.2	0.1
.132	2.33	2.68	103.3	5.5	0.4
Methyl Alcohol M = 3.2 when B + W = 100					
.161	3.94	1.07	105.0	0.4	0.1
.159	3.36	1.64	105.6	0.4	0.2
.161	2.92	2.08	105.4	0.3	0.7
Methyl Alcohol M = 4.0 when B + W = 100					
.166	3.59	.408	81.5	3.8	0.3
.142	2.93	.556	95.6	1.6	0.2
.160	2.97	1.03	99.8	0.3	0.3
.157	2.41	1.59	100.4	1.7	0.1
.160	1.87	2.13	93.5	0.4	0.4
.179	1.72	2.78	82.4	0.5	0.7
Methyl Alcohol M = 5.0 when B + W = 100					
.177	3.15	.353	74.7	0.6	0.8
.175	2.98	.332	88.8	0.6	0.4
.253	3.77	1.24	92.9	1.1	0.6
.251	3.01	1.99	93.0	0.1	0.0
.251	2.52	2.48	89.6	0.4	0.4
.250	2.00	3.00	78.1	0.0	0.5
Methyl Alcohol M = 5.5 when B + W = 100					
.272	3.85	1.15	89.9	1.1	0.0
.275	3.39	1.61	90.4	0.2	0.0
.274	2.95	2.05	89.6	0.4	0.0
Methyl Alcohol M = 6.3 when B + W = 100					
.313	4.31	.692	77.8	1.0	0.3
.316	2.32	2.68	77.1	0.3	0.4
Methyl Alcohol M = 7.2 when B + W = 100					
.360	4.11	.898	76.5	0.3	0.5
.362	2.70	2.30	76.4	0.5	0.1
Methyl Alcohol M = 7.8 when B + W = 100					
.389	3.69	1.31	77.1	0.6	0.5
.389	3.20	1.80	74.9	0.4	0.1

TABLE VII

Binodal Curves at 75°C., 90°C. and 105°C.

B + W = 100

Temp. 75°C. Composition M.	B.
0.0	6.8 and 73.7
2.0	7.4 ” 69.8
4.0	9.1 ” 64.8
5.0	10.6 ” 61.4
6.3	12.7 ” 54.8
7.2	16.6 ” 47.8
7.8	19.5 ” 35.4

Temp. 90°C. Composition M.	B.
0.0	7.8 and 69.8
2.0	9.0 ” 64.5
4.0	13.0 ” 56.5
5.0	16.5 ” 49.0
5.5	23.0 ” 39.5

Temp. 105°C. Composition M.	B.
0.0	9.8 and 64.3
2.0	13.3 ” 56.1
2.5	15.7 ” 52.1
3.2	21.7 ” 42.7

TABLE VIII

Tie Lines at 75°C. and 90°C.

Comp. of system			Phase Weight Ratio	Comp. upper phase			Comp. lower phase		
M.	W.	B.		M.	W.	B.	M.	W.	B.
75°C.									
.615	6.66	3.57	.983	6.0	44.8	55.2	6.8	85.0	15.0
.525	6.78	3.59	.830	4 5	36.8	63.2	5.5	88.7	11.3
.268	6.59	3.51	.758	2.1	30.0	70.0	3.1	92.0	8.0
90°C.									
.213	6.54	3.72	.973	2.00	35.4	64.6	2.20	90.8	9.2
.421	6.66	3.68	1.16	4.10	43 9	56.1	3.92	87.8	12.2

TABLE IX

The Plait Points

Temperature °C.	Composition of system M.	W.	B.
0	18.5	63.1	36.9
15	16.0	64.5	35.5
30	13.9	65.5	34.5
45	11.5	66.0	34.0
60	9.7	66.8	33.2
75	7.8	67.0	33.0
90 (interpolated)	5.6	67.3	32.7
105 (interpolated)	3.5	67.4	32.6
(H&M) 125.15	0	67.5	32.5

TABLE X

The Effect of Methyl Alcohol on the Critical Temperature for Systems containing Constant Amounts of Water and N Butyl Alcohol

Temperature °C.	Composition (B. = 35, W = 65) M.	Temperature °C.	Composition (B. = 35, W. = 65)
0	18.5	75	7.8
15	16.2	90	5.5
30	13.8	105	3.5
45	11.8	110.9	2.4
60	9 8	120.6	1.1
		125.15	0 (H & M)

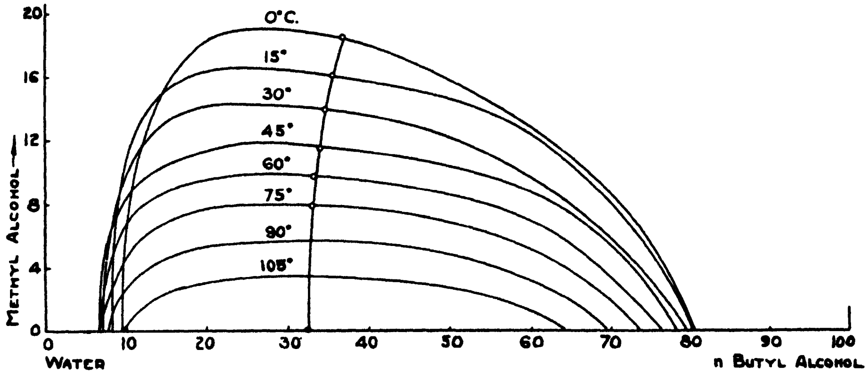

FIG. 1.
Binodal curves and Plait Points

The solubility relations in the binary system n. butyl alcohol-water have been investigated, especially by Jones and by Hill and Malissoff.[8] Their results differ chiefly in the values assigned to the composition of the aqueous phase at low temperatures, the maximum difference occurring at 20°C. When we extrapolated our binodal curves, we obtained a series of values for the composition of this aqueous phase and noted that at 15°C. and 30°C. our values agreed best with those of Hill and Malissoff. At 0°C. and 45°C. where the differences were not so great, our values were a little closer to those of Jones and at temperatures above 45°C., our extrapolation was too inaccurate for us to differentiate between the results of these previous workers. In order to make the comparison, the results of these investigators were plotted and the values taken from the smooth curve drawn. The curve of Hill and Malissoff's results was extrapolated to 0°C. Since our results agreed best with those of Hill and Malissoff at those temperatures where the really significant differences occur, we have used their results for the correlation of our determinations.

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[8] Hill and Malissoff: J. Am. Chem. Soc., **48**, 918 (1926).

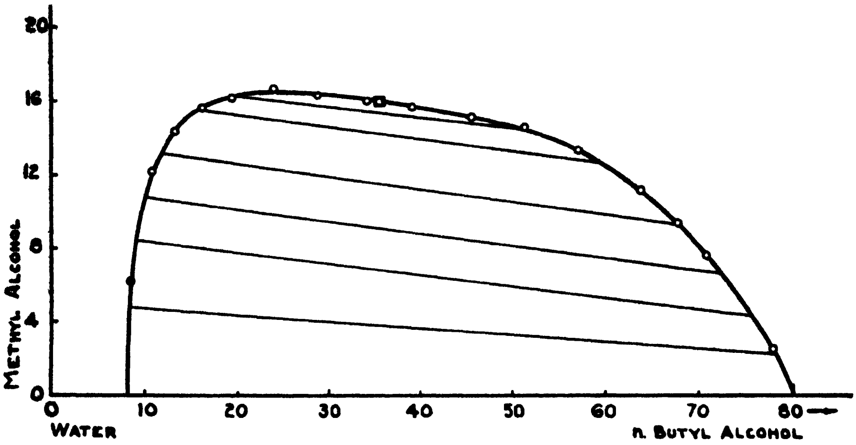

Fig. 2.
Tie lines at 15°C.

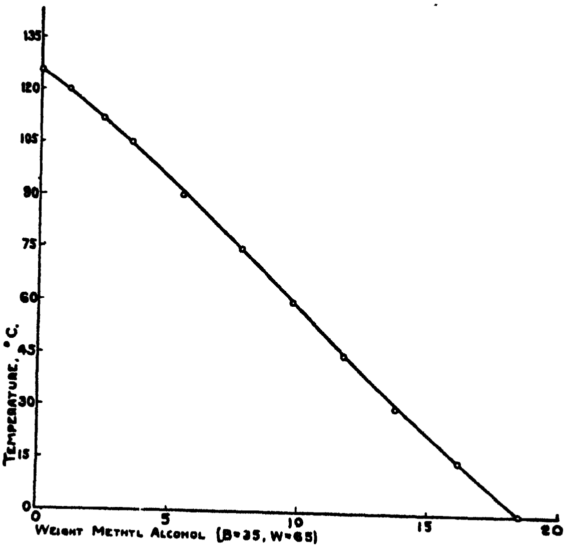

Fig. 3.

In Fig. 1, are given our results for the binodal curves combined with those of Hill and Malissoff for the binary system, n. butyl alcohol-water. An inspection of this graph indicates that the values of the plait points at 90°C. and 105°C. obtained by interpolation cannot be much in error. It seems hardly necessary for us to indicate graphically the various tie lines which we have determined. Perhaps the most useful series would be that obtained at 15°C. which is shown in Fig. 2. The slope of the saturation surface (solid model) at 35 weight percent n. butyl alcohol (B + W = 100) is nearly linear. This is indicated by the plot of the results given in Table X, which is reproduced in Fig. 3.

Summary

The binodal curves, tie lines and plait points of the system n. butyl alcohol-methyl alcohol-water have been determined at temperatures ranging from 0°C. to 105°C. These results have been presented in tabular form and in part graphically.

Certain additional results (particularly densities) which were required for these determinations have been indicated.

Department of Chemistry,
University of Toronto,
January 16, 1931.

A STUDY OF THE REFRACTOMETRIC ESTIMATION OF PROTEINS

I. The Numerical Value of the Refractive Index Constant *a* for Antitoxic Globulins*

BY TILLMAN D. GERLOUGH AND WOODFORD WHITE

The refractive index method for estimating serum proteins, introduced by Reiss,[1] and further developed by Robertson,[2] rests upon a simple linear relationship between concentration and refractive index of the solution. This relationship is expressed by the equation $C = \frac{n - n_1}{a}$, where n and n_1 are the refractive indices of the solution and solvent respectively. C is concentration in grams per 100 cc. of solution, and a is a constant characteristic of a particular protein and is numerically equal to the change in refractive index produced by a change in concentration of 1 gram in 100 cc. When a is expressed in these terms it remains independent of concentration and may, for most purposes, be considered as independent of ordinary temperature changes.

This method has been used extensively in studying serum proteins under normal and pathological conditions, but has received very little attention as a means of measuring accurately the protein content of antitoxins (purified pseudoglobulin solutions prepared from antitoxic horse plasma or serum). It is particularly adapted for such determinations because it is rapid, accurate and entails no loss of material. However, when we first attempted to apply the method to the determination of protein content of antitoxic globulins it did not give results comparable with other reliable methods. We could see no reason why the same general procedure and the refractive index constant employed by many previous workers for the determination of globulin in serum would not give a true measure of the protein content of antitoxic globulin solution. The source of discrepancy was found to be in the value of the constant employed. After the constant was carefully redetermined the results were identical with those obtained by other methods. For instance, in our preliminary work the protein content computed by either of Reiss' constants for pseudo-globulin, 0.00230 or 0.00224, was consistently more than 20 per cent lower than that found by gravimetric, nitrogen, and density determinations. A similar discrepancy was observed by Homer[3] in connection with her work on antitoxins. Miss Homer stated that the protein concentration determined by refractive index through the use of Reiss tables was consistently lower than her gravimetric measurements. Although she apparently made no attempt to check the refractive index constant, it was suggested that the refractive indices of the individual serum proteins required further study.

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*Contribution from the Research and Biological Laboratories of E. R. Squibb and Sons, New Brunswick, N. J.

The purpose of this communication is to present the results of an investigation on the refractive index constant of antitoxic protein as defined by equation $a = \frac{n - n_1}{C}$. The value of *a*, 0.00184, has been established for the following antitoxic globulins: diphtheria, tetanus, scarlet fever and erysipelas.

Purification of the Antitoxins

The antitoxins were first concentrated from horse plasma by a method similar to that described by Banzhaf,[4] and then further purified by removal of remaining euglobulin and denatured protein.[5,6] This was accomplished by diluting the dialyzed* antitoxin with distilled water to 3 per cent protein and adjusting the reaction to pH 5.7 to 5.8. The antitoxin in the clear supernatant liquid was reconcentrated by salting out at pH 7.0 with $(NH_4)_2SO_4$ and the salt removed by pressing the precipitate and dialyzing the solution to a specific conductance of 3 to 5×10^{-5}. A portion of each dialyzed preparation was withdrawn at this stage for measurements of refractive index, density, total solids and nitrogen (Tables I-IV). These antitoxin solutions contained 13 to 16 per cent protein and less than 0.10 mg. phosphorus, 1.5 mg. of ash and 3 to 5 mg. of ether-extractable matter per gram of protein. The remaining portion of each dialyzed solution was further treated by the method of Hewitt[7] by precipitating with an alcohol-ether mixture 70:30 (by volume), extracting with ether and finally drying over P_2O_5. These dried antitoxic globulins were used in the preparation of protein solutions of known concentration, upon which a similar series of measurements was carried out.

Experimental Procedure

All measurements of refractive index and density were made at 25°C. A Zeiss immersion refractometer was employed and scale readings converted into refractive indices. The densities were determined with a pyknometer.

The dialyzed antitoxin solutions, as well as those made up from dried antitoxin, were studied in the presence of suitable electrolyte. Refractive indices of the antitoxic globulin solutions were measured in 0.02 N NaCl. The powdered antitoxins were not completely soluble in dilute NaCl, but dissolved readily in 0.036 NaOH, and were examined in this solvent. Solutions of known protein concentration were prepared by dissolving weighed amounts of the powder in known weights of the NaOH solution.

The protein content of the dialyzed antitoxin solutions was determined by evaporating and drying weighed portions. A sufficient sample to yield 400 to 600 mg. of dried solids was placed in weighing dishes and heated for 5 hours at 110°C. The weighing dishes employed were 7 cm. in diameter. Evaporating surface was increased by spreading 8 cc. of washed and ignited sand on the bottom of each dish. Longer heating or higher temperatures up to 130°C gave the same results. Protein content was also checked in a few instances by coagulation with heat. The coagulum was collected in a Gooch crucible, washed once with alcohol and once with ether, dried at 110°C and weighed. This procedure yielded results identical with those obtained by evaporation and drying.

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*The solutions were dialyzed to a specific conductance of 2.0 to 2.4×10^{-4}.

Refractive index measurements on the two preparations, i.e., the dialyzed solutions and solutions of the powdered antitoxin furnished two series of results based on solids determined by independent procedures. In addition to solids obtained by evaporation and by direct weighing, nitrogen determinations by the Kjeldahl method were made on the solutions and dried antitoxins. All gravimetric and nitrogen determinations were made in duplicate and corrected for any added electrolyte.

Experimental Results

These are collected in Tables I to IV. In this connection it may be stated that the protein concentration, in grams per 100 cc. are not recorded directly in the tables. These values may be obtained by multiplying the percentage of protein by the density of the solution. Not all of the densities found in Table I and III were direct determinations. Some were obtained by graphical interpolation of the data in Table IV. The reaction of all antitoxins employed except those made up in dilute NaOH, was between pH 6.2 and 6.6.

(a) *Dialyzed Antitoxin Solutions.*

In Table I are given the results obtained on dialyzed antitoxin solutions. The protein concentration of solutions in sets (A) and (B) of this table was determined by the gravimetric method while those of set (C) were calculated from nitrogen determinations. The average values for the constant, *a*, obtained from these three sets of determinations are: (A) 0.001834; (B) 0.001839; (C) 0.001834. It should be stated that the solutions of set (B) contained 0.85 per cent NaCl plus 0.5 per cent phenol and that the values of *a* are corrected for a small amount of phenol which was apparently fixed by the protein during the gravimetric determination by direct evaporation. Separate experiments showed that the presence of 0.5 per cent phenol in the antitoxin solutions containing 14 to 16 per cent protein, increased the total weight of dried solids, i.e., protein and salt, by 1.2 per cent. If the phenol corrections were not allowed for, the average value of *a* would be 0.001817.

In addition to the data given in Table I other measurements were made to determine whether or not higher concentrations of solvent salt exert any effect on the refractive index of antitoxic globulin. Antitoxin solutions of the same protein content, 6.5 per cent, were compared in 0.02, 0.04, 0.10 and 1.0 M NaCl and in 1.0 M $(NH_4)_2SO_4$. The refractive index due to the protein alone was found to be identical in all NaCl solutions within the limits of accuracy of the instrument. In 1.0 M $(NH_4)_2SO_4$ the increment was low by 1.0 per cent.

TABLE I

Values of the Refractive Index Constant a for Antitoxic Globulin Solutions

Globulin in N/50 NaCl	Protein Conc. per cent	$n - n_1$	Density $\frac{25°C}{4}$	$a = \frac{n - n_1}{\text{per cent protein} \times d}$
(A) *Protein Concentration obtained by drying to constant weight*				
Diphtheria (1)	16.15	0.03092	1.0435	0.001835
Diphtheria (2)	8.32	0.01554	1.0210	0.001830
Diphtheria (3)	16.18	0.03093	1.0436	0.001832
Diphtheria (4)	11.71	0.02215	1.0308	0.001835
Diphtheria (5)	3.42	0.00630	1.0072	0.001831
Tetanus (1)	9.32	0.01745	1.0238	0.001829
Tetanus (2)	13.74	0.02616	1.0368	0.001831
Erysipelas (1)	6.46	0.01207	1.0157	0.001839
Erysipelas (2)	13.09	0.02485	1.0348	0.001835
Scarlet Fever (1)	8.74	0.01639	1.0222	0.001835
Scarlet Fever (2)	15.68	0.03002	1.0427	0.001837
				Av. 0.001834
(B) *In Saline Salt and 0.50 per cent phenol*				
Diphtheria (1)	14.62	0.02814	1.0438	0.001844
Diphtheria (2)	15.57	0.02987	1.0466	0.001833
Tetanus (1)	14.91	0.02861	1.0460	0.001834
Tetanus (2)	15.81	0.03042	1.0474	0.001837
Erysipelas	14.49	0.02788	1.0434	0.001844
Scarlet Fever (1)	14.43	0.02774	1.0446	0.001840
Scarlet Fever (2)	14.63	0.02812	1.0439	0.001841
				Av. 0.001839
(C) *Protein Concentration calculated from Nitrogen Determinations*				
Diphtheria (6)	8.33	0.01554	1.0202	0.001830
Tetanus (3)	13.23	0.02507	1.0346	0.001832
Erysipelas (1)	6.46	0.01207	1.0149	0.001838
Scarlet Fever (1)	8.73	0.01639	1.0214	0.001837
				Av. 0.001834

TABLE II

Influence of NaOH on the Refractive Index of Antitoxic Globulin

(1) Antitoxic Globulin	(2) Normality NaOH	(3) Per cent Protein	(4) $n - n_1$ in Dilute NaCl	(5) $n - n_1$ in Dilute NaOH	(6) $\frac{(4) - (5)}{(4)}$ in per cent
Diphtheria (7)	0.036	14.70	0.02593	0.02564	1.12
Scarlet Fever (3)	0.036	12.30	0.02186	0.02153	1.50
Tetanus (4)	0.036	9.70	0.01747	0.01717	1.71
Diphtheria (7)	0.036	7.10	0.01282	0.01259	1.80
Diphtheria (7)	0.018	7.10	0.01282	0.01272	0.78
Diphtheria (7)	0.018	14.70	0.02593	0.02578	0.58

TABLE III

Values of the Refractive Index Constant *a* for Solutions of Dried Antitoxic Globulin in Sodium Hydroxide

Globulin in 0.036 N NaOH	Protein Concn. per cent	Density $d\frac{25°C}{4}$	$n-n_1$	$a = \frac{n-n_1}{\text{per cent protein} \times d}$ in NaOH	Correction for Effect of Alkali per cent	*a* (Corrected)
Diphtheria (1)	6.56	1.0163	0.01208	0.001812	1.82	0.001845
Diphtheria (2)	9.25	1.0239	0.01713	0.001809	1.75	0.001841
Tetanus (1)	13.80	1.0367	0.02605	0.001820	1.30	0.001844
Tetanus (2)	7.76	1.0197	0.01435	0.001814	1.79	0.001846
Tetanus (3)	8.92	1.0229	0.01651	0.001809	1.76	0.001841
Tetanus (4)	6.22	1.0154	0.01141	0.001807	1.90	0.001841
Erysipelas (1)	9.65	1.0250	0.01787	0.001810	1.73	0.001841
Erysipelas (2)	7.83	1.0199	0.01443	0.001807	1.80	0.001840
Scarlet Fever (1)	8.92	1.0229	0.01656	0.001815	1.76	0.001847
Scarlet Fever (2)	10.23	1.0265	0.01906	0.001815	1.69	0.001846
						Av. 0.001843

Solutions of Powdered Antitoxin in NaOH

The results obtained on solutions made up with weighed quantities of the powdered antitoxin in a weighed amount of 0.036 N NaOH are shown in Table III. In this table two sets of constants appear, those actually obtained in 0.036 NaOH (Column 5), and the latter values corrected for the decrease in refractive index brought about by the presence of NaOH in the system (Column 7). It will be noted that the observed values are definitely lower than the corrected values. Since this lowering is a function of the concentration both of protein and alkali its magnitude was observed over a range of protein concentrations consistent with working conditions, and the corrections interpolated graphically from calculated deviations in the last column of Table II. In determining these corrections the apparent refractive index of the protein in dilute NaOH was compared with its refractive index in dilute NaCl solution as follows:—Equal weights of the same antitoxin solution were placed in two different flasks. A definite weight of NaCl solution of suitable concentration was added to one flask while an equal weight of NaOH solution of the same refractive index was placed in the other. After mixing, the refractive indices of both solutions were determined under identical conditions. The resulting measurements are set forth in Columns 4 and 5 of Table II.

The average constant of the various dry antitoxins, corrected for the effect of NaOH, is 0.001843. When not so corrected, the average value of this constant is 0.001812.

TABLE IV

Densities of Antitoxic Globulin Solutions at 25°C/4

	Per cent Protein	Density in N/50 NaCl
A. *Antitoxic Globulin Solutions*		
	3.41	1.0072
	5.13	1.0120
	7.71	1.0193
	9.06	1.0231
	9.79	1.0251
	11.71	1.0308
	16.29	1.0441
	0.00	1.00085
B. *Dried Antitoxic Globulin*		
		Density in 0.036 NaOH
	2.73	1.0059
	3.83	1.0089
	6.22	1.0154
	7 18	1.0179
	9.71	1.0251
	13.80	1.0367
	0 00	1.00168

A total of 18 nitrogen determinations were made to ascertain the nitrogen content of the antitoxic globulins. The material used included antitoxic globulins in solution and solid form as well as antitoxic globulin which had been electro-dialyzed to a specific conductance of 6 × 10^{-6} to remove last traces of $(NH_4)_2SO_4$. The average of all nitrogen values was 15.55 per cent. None of the individual determinations deviated more than 0.25 from the average. Our results are considerably higher than those reported by Banzhaf, Suguira and Falk[8] for the nitrogen content of antitoxins and are in better agreement with the value, 15.85 per cent, recorded by Hammarsten[9] and by others for "normal" serum globulin, i.e., from non-immunized horses.

The average refractive index constant obtained on 10 solutions of dried antitoxins, whose protein content was calculated from nitrogen determinations was 0.001844 when corrected for the effect of NaOH.

The average of all determinations, 42 in number, was selected as the final value for the constant a. This value was 0.001839; when rounded, 0.00184.

Table IV shows the densities of solutions of both types of antitoxin preparations. They agree with those recorded by Chick and Martin[10] and Chick[11] for pseudo-globulin (horse), when compared under the same conditions. Solutions of the powdered antitoxins (B) in dilute NaOH gave densities sensibly lower than those observed for the antitoxic globulin solutions (A) in dilute NaCl. In the absence of electrolyte, the densities may be calculated from the following equations: (A) $d\frac{25^\circ}{4} = 0.99708 + 0.002727C + 0.00000602C^2$; (B) $d\frac{25^\circ}{4} = 0.99708 + 0.002611C + 0.0000101C^2$; where C is protein concentration in per cent by weight. The second and third term coefficients were evaluated by the method of least squares. The densities of solvent and protein were regarded as additive.*

Discussion

According to Robertson the refractive index constant a is independent of solvent salts, dilute acids or alkali; in other words, the refractive index of the protein and solvent are additive. Although we found strict additivity in dilute neutral salt solvents when determined in the proximity of the isoelectric point, small but consistent differences observed in alkaline solution lead us to conclude that the refractive indices of NaOH and antitoxin solution are not additive. The magnitude of the deviations from strict additivity depends on concentration both of protein and NaOH or more probably on the amount of NaOH combined. These deviations were large enough to noticeably affect the constant in the third significant figure and thus be of consequence in measurement of antitoxin solutions which contain 15 to 20 per cent protein. Similar observations concerning the effect of solvents have been made by Thomas and Mayer[12] for gelatin in dilute HCl and by Kondo and Hayashi[13] for casein in dilute NaOH.

Since the constant determined by us is approximately 20 per cent lower than Reiss' value it might be argued that the discrepancy is due to a difference between "normal" and antitoxic pseudo-globulin. Measurements on the globulin and albumin of "normal" horse sera show that *this is not true*. The following values were obtained:—euglobulin,** 0.001845; pseudo-globulin, 0.001843; albumin, 0.001840. Many other measurements were made on the protein fractions separated by various procedures, but in no instance could we detect any significant difference in refractive index between the globulins and albumin of "normal" unheated and heated antitoxic plasmas or serums. Concentrated pneumococcus antibody*** also gave essentially the same value, viz., 0.001845.

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*In separate experiments it was found that the densities of protein and alkali are not strictly additive.

**Precipitated by 33⅓ per cent of saturation of $(NH_4)_2SO_4$.

***Precipitated from serum by diluting 1:12 with distilled water and adjusting the reaction to pH 6.8 according to the methods of Felton (14) (15).

The recent work of von Deseö[16] shows that the constant for purified globulin lies between 0.00174 and 0.00189. Our results agree more nearly with his. An interesting observation brought out by von Deseö's measurements and one which has important bearing on the value of the constant if determined in high concentration of $(NH_4)_2SO_4$ solution following fractional precipitation of a serum, was that the precipitate binds water[17] and thus concentrates the salt in the filtrate.* Because of this concentration of salt the apparent constant obtained will vary depending on the amount precipitated, and, in the case of globulin, appear to be larger than when determined in the same solvent salt of concentration insufficient to cause precipitation.

Summary

1. The increment in refractive index corresponding to a change of protein concentration of 1.000 gram in 100 cc. of solution has been accurately determined for four antitoxic globulins and "normal" serum globulins of the horse. The value of this increment (constant *a*) for protein concentrations between 3 and 17 grams per 100 cc. is 0.00184.

2. NaOH produced a small but definite lowering in the refractive index of the protein.

Bibliography

[1] E. Reiss: Archiv. Exp. Path. and Pharmakol., **51**, 19 (1914).
[2] T. B. Robertson: "The Physical Chemistry of the Proteins" (1920).
[3] A. Homer: J. Soc. Chem. Ind., **38**, 145T (1919).
[4] E. J. Banzhaf: "Collected Studies," Bur. Lab. Dept. of Health, New York City, **7**, 114 (1912).
[5] H. Chick: J. Path. and Bacteriol., **19**, 131 (1914-1915).
[6] P. P. Murdick: J. Immunol., **17**, 269 (1929).
[7] L. F. Hewitt: Biochem. J., **21**, 216 (1927).
[8] E. J. Banzhaf, K. Suguira, and K. G. Falk, J. Immunol., **2**, 125 (1916).
[9] O. Hammarsten and S. J. Hedin: "Physiological Chemistry" (1914).
[10] H. Chick and C. J. Martin: Biochem. J., **7**, 92 (1913).
[11] H. Chick: Biochem. J., **8**, 261 (1914).
[12] A. W. Thomas and C. W. Mayer: Proc. Soc. Expt. Biol. Med., **25**, 667 (1928).
[13] K. Kondo and T. Hayashi: Bull. Agr. Chem. Soc. Japan, **2**, 147 (1926).
[14] L. Felton: J. Inf. Dis., **37**, 199 (1925).
[15] L. Felton: J. Inf. Dis., **43**, 543 (1928).
[16] D. von Deseö: Biochem. Z., **217**, 196 (1930).
[17] S. P. L. Sörensen: J. Am. Chem. Soc., **48**, 457 (1925).

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*We have confirmed this observation.

THE SOLUBILITY OF BARIUM SULPHATE IN SULPHURIC ACID

BY NELSON R. TRENNER[1] AND H. AUSTIN TAYLOR

The high solubility of barium sulphate in absolute sulphuric acid and its marked decrease on addition of water presents a real anomaly when considered from the point of view of modern theories of strong electrolytes whilst realising that the dielectric constant of absolute sulphuric acid is of the same order as that of water. A search of the literature for reliable data on the system revealed a complete lack of concordance among the results of many investigators, not only in the solubility of the salt in the pure acid but more particularly in the solid phases in equilibrium with aqueous sulphuric acid solutions.

Kendall and Davidson[2] attempted to isolate the solid phase by freezing it from solution and drying between porous plates. They find an analysis corresponding to $BaSO_4.3H_2SO_4$. Barter[3] attempted to analyse the wet solids and the saturated solutions deducing the composition of the solid by graphical extrapolation, obtaining two compounds $3BaSO_4.8SO_3.7H_2O$, stable from 85.5 to 93 percent sulphuric acid and $4BaO.5SO_3.6H_2O$ stable in high concentrations. The latter stable at high concentrations of acid having an excess of water, whilst the former stable at lower concentrations, an excess of SO_3 is almost beyond credence. The difficulty no doubt lies in the handling of so viscous and hygroscopic a system where experience shows that exposure to the atmosphere even for a very short period renders an analysis worthless.

An attempt was made therefore to determine the true solubility relationships between $BaSO_4$, H_2SO_4 and H_2O with as reasonable a degree of accuracy as such a system would permit.

Experimental

Preparation of Materials.

1. Sulphuric Acid. Absolute sulphuric acid was prepared by two different methods which gave consistent results. In the first method a pure nitrogen and arsenic free acid was redistilled at a pressure of 1-2 mms. of mercury yielding about a 95 percent acid. To bring this up to absolute acid, purified fuming sulphuric acid was distilled into it until its concentration was correct as determined by specific gravity methods. Careful volumetric analyses were then made. In the second method a slightly fuming sulphuric acid prepared from redistilled acid and sulphur trioxide, was brought down to absolute by addition of water. The change in resistance of the acid at constant temperature, was meanwhile measured. According to Lichty[4] the resistance of absolute acid is a maximum. Subsequent analyses showed the acid to be 100 percent within 0.05 percent.

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[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Master of Science at New York University.

[2] J. Am. Chem. Soc., 43, 979 (1921).

[3] Trans. Roy. Soc. Canada, 7, 208 (1913).

[4] J. Phys. Chem., 11, 238 (1907); J. Am. Chem. Soc., 30, 1834 (1908).

2. Barium Sulphate. Barium chloride recrystallised three times was used to precipitate barium sulphate from pure sulphuric acid. The possible impurities could then be only barium chloride, hydrogen chloride or sulphuric acid. Of these the two latter seem to be strongly adsorbed since after washing continuously with hot water until the wash water showed no acidity to methyl orange, upon roasting, copious fumes of hydrogen chloride and sulphur trioxide were evolved. To remove the first two the sulphate was redissolved in absolute sulphuric acid and maintained at about 200°C. for not less than half an hour. The supernatant liquid was drawn off and cooled, no crystallisation taking place. When cold, this solution was poured into a very large volume of cold distilled water yielding barium sulphate with no other possible impurity than sulphuric acid. Since the decomposition of $BaSO_4$ only becomes apparent above 900°C., the sulphuric acid, admixed or adsorbed, was removed by roasting at about 600°C. for from 18 to 24 hours. Different preparations yielded samples of different particle size. Some fine-grained samples were obtained by pulverising in an agate mortar and required nine days to settle completely from solution as compared with less than twenty-four hours for the usual samples.

Method of Measurement. The solubility determinations were made on various mixtures of barium sulphate, sulphuric acid and water which had been allowed to come to equilibrium in sealed tubes by rotation for seven days in a thermostat at 25 ± 0.05°C. The ternary complexes were prepared by placing a known weight of the salt in the tube which had two openings: one, a fine capillary as an air vent, the other carrying a constricted tube with a ground joint and stopper, also fitting a Lunge pipette from which the acid-water mixtures could be forced with dry air. The acid solutions were made up by drawing into the pipette a calculated amount of absolute acid and water, each being weighed. The weight of the acid-water mixtures run into the solubility tube having been determined, the capillary and constricted side tubes were sealed off, the whole procedure occurring in an atmosphere of dry air. Three weighed samples of acid were taken at each filling for check determinations by titration of the acid concentration.

Equilibrium being established in the tubes the solutions were allowed to settle for twenty-four hours, the supernatant liquid being then drawn into a Lunge pipette for analysis. The titration of the acid in the saturated solution was made using carbonate-free sodium hydroxide with methyl orange as indicator. The titration had to be performed in the presence of solid barium sulphate thrown down by dilution with water. The end-points were matched with a color standard adjusted for opacity by addition of about the average amount of suspended barium sulphate. Weighed samples were drawn from the pipette for titration and also for the gravimetric analyses of the sulphate. Check determinations were made for every measurement.

Experimental Results and Discussion

The results obtained by the above method are given in detail in Table I.

TABLE I

Initial Complex			Saturated Solution			Conc.	Solid Phase
H_2SO_4	H_2O	$BaSO_4$	H_2SO_4	H_2O	$BaSO_4$	H_2SO_4	H_2SO_4
			A				
82.92	—	17.08	84.11	—	15.89	100.00	—
—	—	—	—	—	15.77	99.81	—
74.87	0.14	24.99	84.05	0.21	15.74	99.75	67.33
83.85	0.16	15.99	84.22	0.17	15.61	99.80	—
—	—	—	—	—	15.68	99.70	—
—	—	—	—	—	15.22	99.61	—
—	—	—	—	—	14.79	99.45	—
62.92	0.21	36.87	84.84	0.46	14.70	99.47	—
—	—	—	—	—	13.84	99.07	—
69.78	0.52	29.71	85.27	0.90	13.83	99.95	—
78.94	0.57	20.49	85.49	0.89	13.62	98.97	68.86
62.87	0.61	36.52	85.80	0.95	13.25	98.91	—
84.00	1.12	14.88	85.57	1.26	13.17	98.65	—
73.94	0.60	25.47	86.00	1.21	12.79	98.61	62 09
77.99	1.16	20.84	86.06	1.65	12.29	98.12	58.86
84.10	1.60	14.29	86 54	1.78	11.68	97.99	62.38
80.37	1.60	18.03	87.22	1.83	10.95	97.80	32.70
81.23	2.63	16.15	88.45	3.02	8.53	96.70	32.55
85.06	3.47	11.47	88.86	3.63	7.05	96.08	—
60.55	1.89	37.56	89.13	3.58	7.29	96.14	28 60
73.26	2.84	23.90	89.28	3.86	6.86	95.85	28.68
—	—	—	89.68	4.53	5.79	95.19	—
75.28	3.97	20.75	90.40	4.97	4.63	94.79	15.24
			B				
78.07	3.67	18.26	90.57	5.33	4.10	94.44	50.43
—	—	—	90.58	6.91	2.51	92.91	—
77.69	5.42	16.89	90.75	7.27	1.97	92.58	39.37
69.46	9.07	21.47	87.45	12.06	0.486	87.96	14.87
69.40	9.12	21.49	85.90	13.87	0.230	86.10	37.70
68.10	9.10	22.80	85.50	14.29	0.210	85.63	37.60
73.25	11.26	15.49	84.93	14.87	0.203	85.08	36.80
—	—	—	—	—	0.058	83.62	—
68.98	13.80	17.23	83.21	16.74	0.050	83.25	2.21

The values in the above table are expressed in percent by weight. The concentration of sulphuric acid is expressed as the ratio of sulphuric acid to sulphuric acid plus water in the saturated solution. Fig. 1 shows the solubility of barium sulphate plotted against the concentration of sulphuric acid in the saturated solution.

In the last column in Table I the percentage of sulphuric acid in the solid phase was obtained by a mathematical extrapolation of the tie-line joining the composition of the initial complex with that of the saturated solution which it yields. To this end it was assumed that the solid phase extracts no water from the solution phase, sulphuric acid alone being possibly removed. The assumption appears to be justifiable in the concentration range studied, where the acid actually possesses a sulphur trioxide vapor pressure. The theoretical percentages of sulphuric acid in possible compounds of the formulae $BaSO_4.H_2SO_4$, $BaSO_4.4H_2SO_4$, and $BaSO_4.5H_2SO_4$ are 29.67, 62.72 and 67.79 respectively. An examination of the data would at first sight suggest that all these compounds are present in the solid phase at certain acid concentration but a reference to Fig. 1 shows no apparent transitions as evidenced by a change in direction of the solubility curve. We are led therefore to consider in more detail the accuracy of the data and more particularly the reliability of the extrapolation.

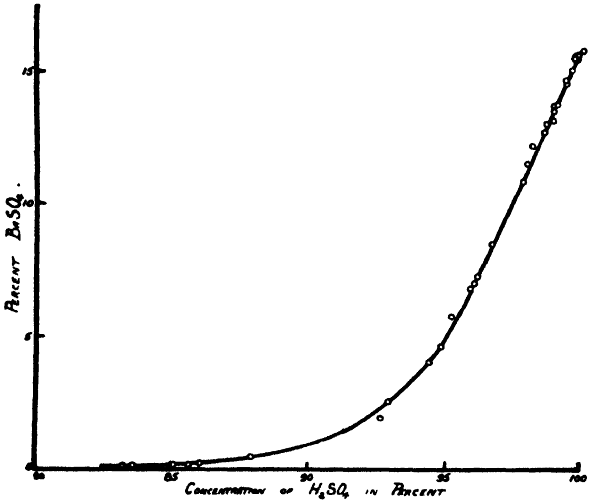

Fig. 1

It is obvious that since the quantity of water both in the initial complex and in the saturated solution is in all cases much less than the quantity of sulphuric acid that the greatest error involved in the extrapolation will be due to an error in these two values for the water. At the higher concentrations of acid this error naturally will be less than at lower acid concentrations and we might expect a greater reliability of the extrapolation under the former conditions. In fact, a complete analysis of the probable error, which need not be detailed here, shows that for acid around 88 percent of the saturated solution the probable error in the extrapolated percentage of acid in the solid phase is of the order of four percent, whereas at 85 percent acid with now only 0.3 to 0.4 percent water the error may be as high as forty percent, despite the previously mentioned care in all volumetric and gravimetric determinations.

In part A of Table I there are four values of the percentage of sulphuric acid in the solid phase in the neighborhood of 30, namely 32.70, 32.55, 28.60 and 28.68 or a mean of 30.6 which might be compared with the 29.67 percent calculated on the basis of $BaSO_4.H_2SO_4$ suggesting a compound of this type as the solid phase. Values below this for example the 15.24 percent quoted might correspond to a mixture of $BaSO_4$ and $BaSO_4.H_2SO_4$. The values above 30 percent as the analysis shows are unreliable and no conclusion can justifiably be drawn concerning compounds with excess sulphuric acid despite the apparent agreement between the extrapolated values and those above mentioned for $BaSO_4.4H_2SO_4$ and $BaSO_4.5H_2SO_4$. If therefore the compound $BaSO_4.H_2SO_4$ should exist a transition from the unsolvated salt should appear in the solubility curve. From the data this would be expected at around 88 percent sulphuric acid which reference to Fig. 1 will show to be on the flat portion of the curve where a break would be very difficult to realise. Its apparent absence cannot be judged then as indicating the non-existence of the compound.

In order therefore to settle definitely the existence of this compound and to determine the exact invariant area in the three-component diagram it was decided to follow the change in a property of the system as the concentration of one of the components was gradually increased. According to the phase rule such a system undergoing a transition of solid phases is invariant and any property of the system will remain constant throughout this process. The limits of constancy of the property then becomes the limits of the invariant area. The property chosen for study was the conductance and the component to be successively increased was water, the determinations of Lichty having shown that as small an amount of water as 0.01 percent gave a measurable change in the conductance of sulphuric acid in the region around absolute acid.

The cell used in these measurements consisted of a pyrex tube carrying electrodes of heavy platinum foil about one square centimeter area and about 40 cms. apart, dimensions chosen to give a conveniently measurable resistance range. Experience showed that for a sharp null point a heavily platinised surface was necessary. The opening in the cell, for the purpose of introducing the various components, carried a wide tube giving free space to allow mixing during tumbling in the thermostat. This tube was closed with a ground-glass stopper and as further protection against water leakage during immersion the whole was covered by a cap ground to fit the outside of the tube.

The resistance of the cell was measured using the usual Wheatstone bridge arrangement, a specially constructed vacuum tube Hartley type oscillator producing a smooth 1000 cycle note being used as source of current. The oscillator was located some ten feet away from the cell and carefully shielded and grounded to minimise extraneous capacity effects. The reliability of the measurements may be illustrated by a comparison of the specific conductivity of absolute sulphuric acid found namely 1045×10^{-6} ohms^{-1} with that found by Lichty, 1040×10^{-6} as the mean of several samples.

The procedure consisted in introducing absolute sulphuric acid, using all the precautions against water absorption mentioned previously, into the weighed conductivity cell and reweighing to show the amount. The conductivity at 25°C was then measured to check the acid concentration. After drying and reweighing, the requisite amount of barium sulphate was added and the whole reweighed. The cap was then secured in place with a rubber jacket and the whole cell rotated in the thermostat until successive conductivity readings gave the same result indicating the establishment of equilibrium, a process requiring not more than 18 hours. The tube was then again dried and reweighed as a check against water absorption, between 0.25 and 0.5 gram conductivity water introduced and the whole reweighed and returned to the thermostat, a process repeated at about 24 hours intervals throughout the entire range of water concentration desired.

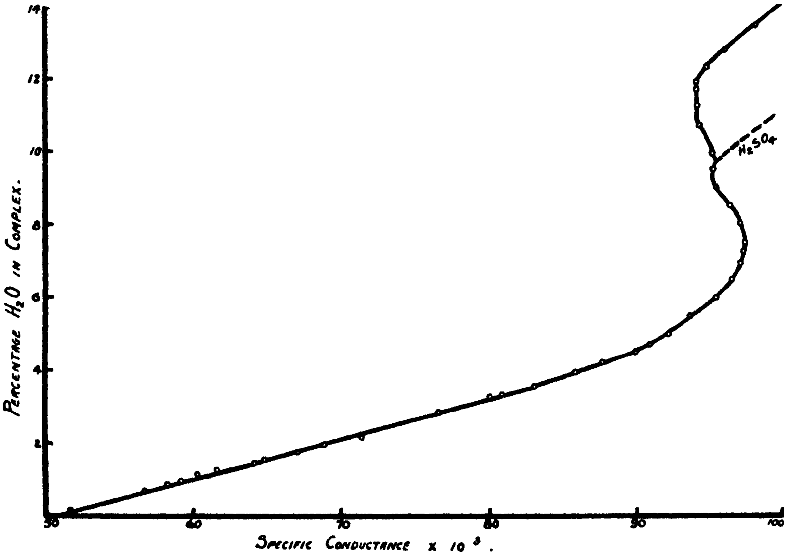

FIG. 2

The values of the specific conductance at various water concentrations are given in Table II, and shown graphically in Fig. 2.

A second cell was also used with a slightly different initial complex which unfortunately developed a leak before the run was completed. The data obtained however checked the above figures when due allowance was made for the slight difference in amount of the solid phase present. The general shape of the curve is in agreement with that for sulphuric acid alone, which has been accounted for by the existence of hydrates. The *S* in the curve occurs at 84.80 percent acid which would correspond to $H_2SO_4.H_2O$. The constancy of the starred values in the Table would indicate an invariance of the system at this point only, since over the remainder of the region covered

TABLE II

Initial Complex		81.54% H_2SO_4, 18.46% $BaSO_4$	
Percent Water	Sp. Cond.	Percent Water	Sp. Cond.
0.000	4889×10^{-5}	5.468	9363×10^{-5}
0.136	5135	5.992	9535
0.722	5681	6.498	9649
0.897	5831	6.980	9710
0.961	5925	7.280	9725
1.103	6030	7.512	9731
1.241	6161	8.044	9700
1.454	6420	8.528	9645
1.542	6486	9.026	9540
1.777	6719	9.496	9520
1.952	6880	9.988	9520
2.190	7142	10.740	9430
2.806	7663	11.256	9420*
3.328	8081	11.760	9418*
3.584	8300	11.941	9418*
3.982	8585	12.390	9495
4.202	8763	12.834	9608
4.532	8990	13.502	9816
4.698	9092	14.111	10000
4.988	9215		

there is a gradual change in conductance with change in water concentration. This constancy would indicate the presence in the system of another compound besides $BaSO_4$, probably an acid solvated barium sulphate.

The composition of the initial complex used and the quantities of water added, being known, the composition of the invariant complex may be calculated. An analysis of the invariant solution then would yield sufficient data to locate the invariant area and thus by extrapolation, the composition of the solid phases in equilibrium. Fig. 3 shows the graphical extrapolation.

It will be observed that the lower limit of the invariant area does not correspond with pure $BaSO_4$ as the solid phase but gives a solid containing about ten percent acid. This is believed to be due to adsorption which though suspected in earlier work, could not be definitely shown. It is for that reason that the data in Table I were divided into two sections A and B, in the former a coarse grained barium sulphate being used, in the latter an extremely fine grained sample and it was this which was employed in the conductance measurements. The last results in section B of Table I where a somewhat lower acid concentration was used gives an extrapolated solid phase containing 2.21 percent acid indicating clearly a gradual and continuous change in composition of the solid phase below about 85 percent acid, characteristic of adsorption.

Such adsorption would cause a displacement of the invariant area as the diagram shows. The extrapolation of the upper limit of the area gave a solid phase of 36.80 percent acid. This is to be compared with the other values in section B of Table I namely 39.37, 37.70 and 37.60, values which would appear to correspond most closely with $BaSO_4.3/2\ H_2SO_4$. However in section A are found values of 32.70, 32.55, 28.60 and 28.68 percent acid in the solid phase which correspond rather well with 29.60 percent acid in $BaSO_4.H_2SO_4$. Realising that the grain size in the latter is much larger than in the former, and hence that the adsorption is probably much less, it must be concluded that the only compound present is probably $BaSO_4.H_2SO_4$, apparent variations from this being due to adsorption. An analysis of the invariant solution showed it to contain a concentration of sulphuric acid of 85.08 percent. A transition occurs in the system therefore at this point.

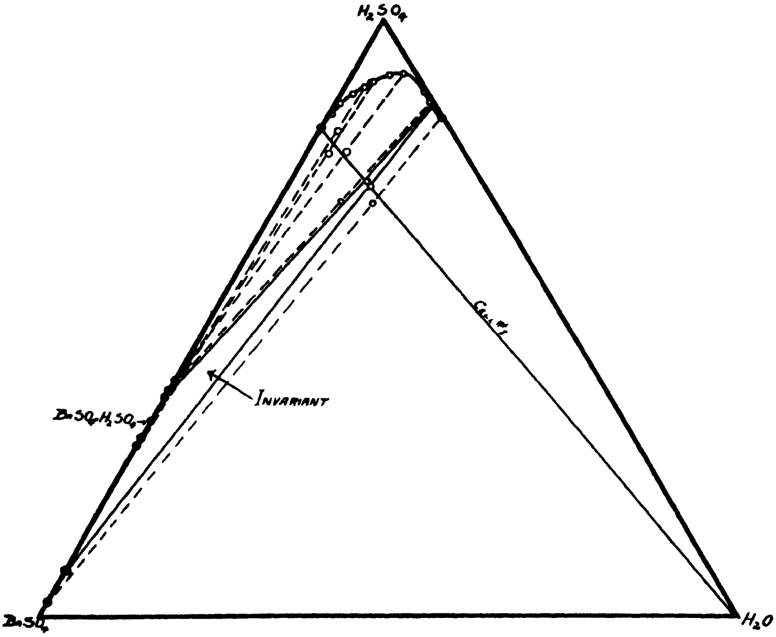

FIG. 3

In conclusion it may be stated that the system shows a marked metastability. In the early stages of the conductance measurements it was observed that in about two hours the equilibrium had reached almost 95 percent completion but that at least eighteen hours were necessary before constant conductance was attained. Furthermore in the data in section B Table I one sample gave an extrapolated value for the acid content of the solid phase of only 14.87 percent. This sample had been agitated in the thermostat for only eighteen hours. The other values shown were obtained from samples agitated not less than five days and show values in the neighborhood of 38 percent. A distinct change also was to be observed in the state of the solid phase after long agitation, the typical opaque white granules of $BaSO_4$ yielding finally well-formed translucent needles. The acid salt therefore would appear to be slow in forming. This metastability together with the complications of adsorption are probably responsible for the lack of a greater concordance than was found in view of the extreme precautions taken throughout the whole work.

Summary

1. The solubility relations for the system $BaSO_4$-H_2SO_4-H_2O at 25°C have been determined over the concentration range 83-100 percent acid. The solubility in absolute acid is 15.89 percent by weight.

2. The system possesses but two solid phases at 25°C $BaSO_4$ and probably $BaSO_4.H_2SO_4$ with a transition at an acid concentration in the neighborhood of 85 percent.

3. The existence of compound formation as distinct from solid solution and adsorption has been demonstrated by the application of a conductance method which might prove convenient and precise in other similar work.

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PHENACETIN HYDROCHLORIDE*

BY IRENE H. SANBORN

Although phenacetin itself is a well known antipyretic, its hydrochloride is rather an elusive substance. Apparently there was no reason to question its accessibility; thus when its existence became a matter of interest in connection with the work on Phase Rule Studies on the Proteins by Wilder D. Bancroft and C. E. Barnett,[1] the author proceeded with the usual methods for such an organic preparation.

Phenacetin is para ethoxy phenyl acetanilide, $C_2H_5OC_6H_4NHC_2H_3O$. From the behavior of the nitrogen atom in analogous compounds, Bancroft and Barnett stated in part that phenyl groups decrease the reactivity of the nitrogen; ethoxy groups increase it; adjacent carbonyl groups decrease it; and alkyl groups increase it. Acetanilide is a weak base but does combine with hydrogen chloride, while diacetanilide, with the diketo linkage, does not. No statement was found in the literature regarding the hydrochloride of benzanilide, $C_6H_5NHCO.C_6H_5$; so Bancroft and Barnett tested it to find that it did form a definite hydrochloride. They concluded that "phenacetin should be at least as positive as acetanilide and therefore must add on hydrogen chloride, although Meyer and Jacobson do not mention the fact."

Accordingly, three attempts were made to prepare the hydrochloride. Phenacetin is a stable, white, crystalline substance of m.p. 135°C, insoluble in cold water, slightly soluble in hot water, and soluble in hot concentrated hydrochloric acid.

A sample was dissolved in hot absolute alcohol, and dry hydrogen chloride gas was passed into the solution. Although the solution was placed in an ice bath, no precipitate appeared. Either the phenacetin hydrochloride was not formed, or else it was dissolved in absolute alcohol.

Another sample was dissolved in an alcohol-ether solution, containing just enough alcohol to keep the phenacetin in solution. The solution was kept cold, and dry hydrogen chloride passed into it as previously. A curdy white precipitate formed, apparently the hydrochloride. In attempting to filter and wash this precipitate, decomposition was evidenced immediately, and phenacetin was recovered on the filter paper.

One other method was tried. Phenacetin was melted, and to the melt concentrated hydrochloric acid was added. The mass was heated, and allowed to stand in a desiccator over stick sodium hydroxide. A white powdery layer formed on the surface of the melt. Probably this was the hydrochloride, for upon exposure to the air it began to fume, and left a residue of phenacetin.

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*This work is a part of the programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] J. Phys. Chem., **34**, 753 (1930).

From these procedures it appeared rather evident that there is such a compound as phenacetin hydrochloride, and that it is exceedingly unstable. For this reason, other methods, whereby the hydrochloride would not be exposed to the air, were used.

The apparatus used in Phase Rule Studies[1] was employed. Phenacetin was pulverized and dried over concentrated sulphuric acid in a desiccator for several days. A sample was placed in the reaction flask, the system was evacuated, and dry hydrogen chloride was introduced. Our data show conclusively that phenacetin combines stoichiometrically with dry hydrogen chloride mol per mol. See data Fig. 1 and Table I.

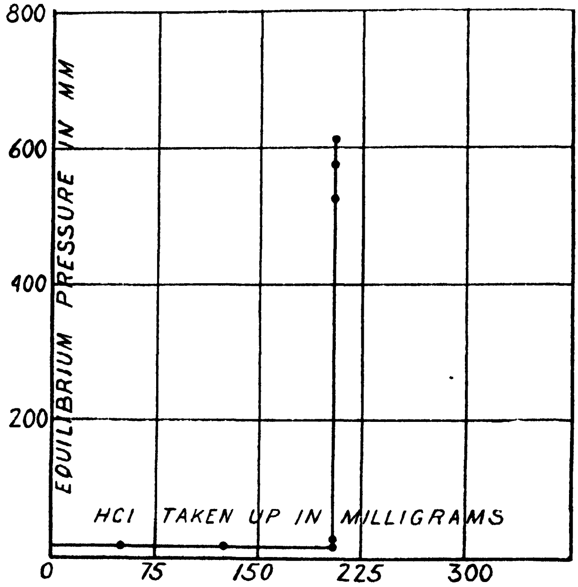

Fig. I

Phenacetin Hydrochloride

TABLE I

Phenacetin and Hydrogen Chloride

	S.T.P.		Sample 2.5 grams		Dry		
Vol HCl added c.c.	Vol HCl removed c.c.	Net volume c.c.	Equilibrium pressure mm.	Vol HCl remaining c.c.	Vol HCl taken up c.c.	Wt. HCl taken up mgm.	Wt. HCl taken per g. mgm.
575.2		575.2	614	262	313.2	512	205
	17.1	558.1	576	246	312.1	508	204
	21.8	536.3	526	224	312.3	508.1	204
	172.4	363.9	25	48	315.9	515	206
	19.2	344.7	17	32.6	312.1	508	204
	1120.4	224.3	17	32.6	191.7	312.3	125
	115.0	109.3	17	32.6	76.7	125	50

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[1] J. Phys. Chem., 34, 449 (1930).

Theoretically one gram of phenacetin should take up 204 mgms. of hydrogen chloride for the formation of phenacetin hydrochloride. We find that it actually does take up that amount. The hydrochloride is a practically colorless fine powder with a dissociation pressure of 17 mm. It melts sharply at 154°C at 741 mm. pressure, and decomposes immediately and completely in water into hydrogen chloride, and the flakey lustrous white phenacetin which gives a m.p. of 135°C. Some of the phenacetin hydrochloride was preserved in a closed tube and its properties tested about five months after its preparation. It was found to be quite stable. Another part was left in an open tube. During this same period this portion slowly decomposed. The surface layer gave a m.p. of 135°C indicating its decomposition into phenacetin and hydrogen chloride.

In order to obtain a separate proof of the existence of phenacetin hydrochloride, a method somewhat similar to the one used by T. W. Richards[1] to establish the identity of $BaCl_2.2H_2O$ was tried. For this experiment a special glass tube was used, so constructed that the sample and solvent could be introduced through A, and into which was sealed a long tube B with a flanged mouth which reached nearly to the bottom of the tube. See Fig. 2. This arrangement made it possible to bring the entire sample in contact with the dry hydrogen chloride. The tube is of such a size that it rests unhampered upon the pan of the ordinary analytical balance.

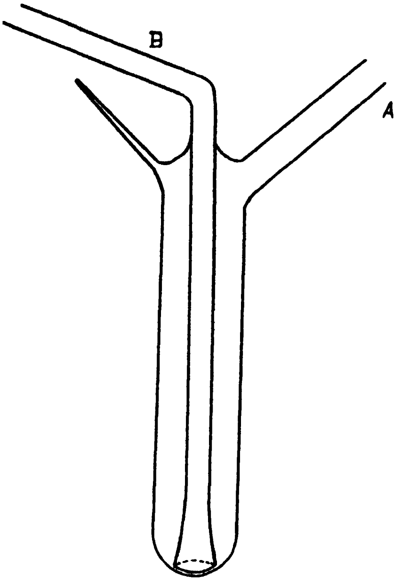

Fig. 2
Glass Drying Tube

TABLE II

Phenacetin Hydrochloride (Curve A)

Sample of phenacetin 0.480 grams.

Wt. HCl taken up mgms.	Time Hours	Time Days	Equivalence in HCl mol per mol.
351	24	1	3.6
80	48	2	.8
56	168	7	.7
56	192	8	.7
56	240	10	.7

Note: 1 equivalent for this sample is 97 mgms.

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[1] Z. anorg. Chem., **17**, 165 (1898).

The sample of finely divided dry phenacetin was placed in the special tube. 25 cc. of freshly distilled dry chloroform was added to the sample. The tube was gently heated to dissolve the phenacetin; after which dry hydrogen chloride was passed through B into the solution. During this process the tube was retained in a bath of warm water until the chloroform had been completely evaporated. The tube was then placed in a desiccator containing concentrated sulphuric acid and stick sodium hydroxide, being removed periodically for the purpose of weighing. The data for two samples are found in Fig. 3 and Tables II and III.

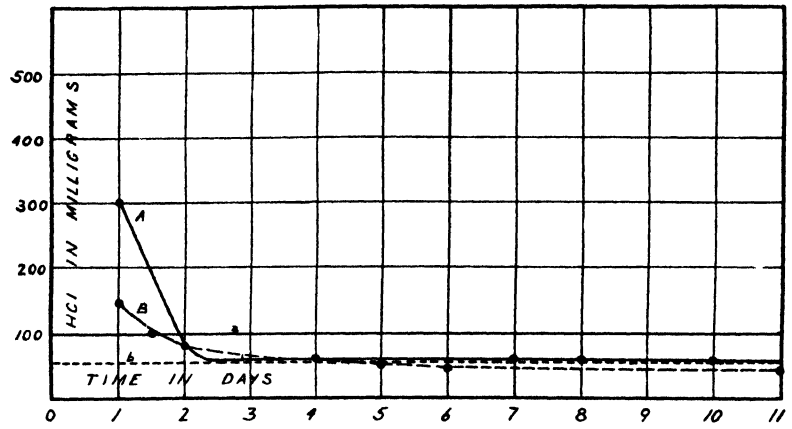

FIG. 3

Dissappearance of HCl from Phenacetin Hydrochloride

TABLE III

Phenacetin Hydrochloride (Curve B)

Sample of phenacetin 0.265 grams.

Wt. HCl taken up mgms	Time		Equivalence in HCl mol per mol.
	Hours	Days	
147	24	1	2.7
99	36	1.5	1.8
57	96	4	1.05
50	120	5	.92
44	144	6	.80
44	264	11	.80

Note: 1 equivalent for this sample is 54 mgms.

The intersection of the line "a" with the curve A represents the point at which the sample contains one equivalent of hydrogen chloride. There should be a break in curve A at this point. As shown, there is none; but there are no points between one and two days and between two days and four days. Consequently the curve as drawn may not be right. To check this a second experiment was done. The intersection of the line "b" with the curve B represents the point at which the sample contains one equivalent of hydrogen chloride. In this case the break comes pretty fairly well at the right place, the loss being about 17 mg. per day from 1.5 to 4 days and 7 mg. per day from 4 to 5 days. Neither curve A nor curve B becomes theoretically horizontal at any point; but the rate of diffusion happens to be very low. The method is not especially accurate in its present form; but it does show conclusively the existence of a definite chemical compound with a composition pretty close to the monohydrochloride.

Another experiment was devised of a similar nature. A weighed sample of the finely divided dry phenacetin was spread upon a weighed watch-glass, thoroughly moistened with concentrated hydrochloric acid, and placed in a vacuum desiccator containing concentrated sulphuric acid. The desiccator was evacuated, and then filled with dry hydrogen chloride. After allowing the sample to remain in the desiccator long enough to insure the complete removal of any trace of water, the sample was removed and weighed. The amount of hydrogen chloride with which it had combined was calculated. The experiment was done twice, using first a small sample of phenacetin, 0.361 g.; and second a larger sample, 2.954 g. The same watch glass was used in each case. After standing in desiccator for a week, at which time all the water had been removed, sample 1 had combined with 0.062 gms. of hydrogen chloride, an amount equivalent mol per mol to 0.84 mol of hydrogen chloride. Sample 2 remained in desiccator for over a month. Upon removal and subsequent weighing it had combined with 0.555 gms. of hydrogen chloride, an amount equivalent to 0.924 mol of hydrogen chloride. See Table IV.

TABLE IV

	1	2
Phenacetin samples	0.361 grams.	2.954 grams.
Amount HCl combined after one week.	0.062	
Amount HCl combined after one month.		.555
Equivalence to HCl mol per mol.	0.84	0.924

The results are conclusive as to the existence of a definite chemical compound; but the results are not such as to lead one to prefer this method to the one in which the pressure is studied. The last two methods have the advantage that there are no stop-cocks to leak and spoil the experiment near the end of a run.

Conclusions

1. Phenacetin combines stoichiometrically with hydrogen chloride mol per mol to form phenacetin hydrochloride.

2. Phenacetin hydrochloride exists as a stable compound in the presence of hydrogen chloride gas. It is a very pale yellow powder with a m.p. of 154°C.

3. At room conditions, phenacetin hydrochloride is unstable because of the dissociation pressure of about 17 mm. It decomposes gradually to give hydrogen chloride and phenacetin.

4. In aqueous solution its decomposition is immediate into phenacetin and hydrogen chloride.

5. While it is possible to show the existence of a compound between phenacetin and hydrogen chloride by passing hydrogen chloride into a solution of phenacetin and ether, the compound cannot be obtained both pure and dry in the ordinary way.

6. The phenacetin hydrochloride has been analyzed indirectly in three different ways, just to show how the problem can be solved.

7. The existence of phenacetin hydrochloride is in accordance with the criteria laid down by Bancroft and Barnett.

Cornell University.

A NEW CELL FOR ELECTRODIALYSIS*

The usual apparatus for electrodialysis consists of three compartments, one for the solution to be dialyzed and one for each of the electrodes. The electrode compartments are commonly as large as the center compartment. The apparatus described in this paper, constructed in line with a suggestion by Kruyt that the electrode compartments be as small as possible, has reduced them to a mere moving film of water.

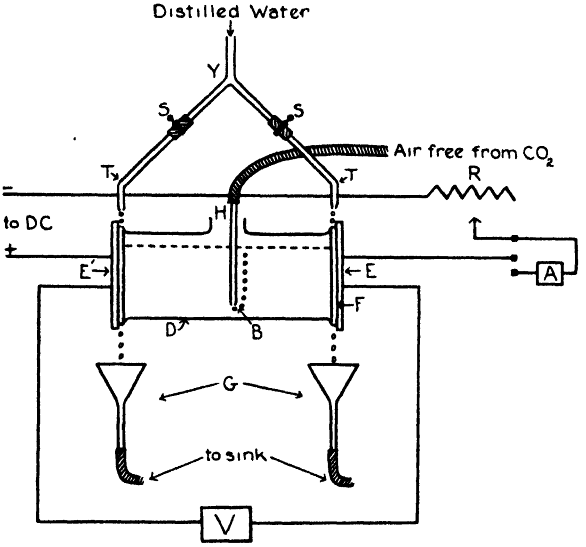

FIG. 1

APPARATUS. The apparatus and electrical connections are shown in Fig. 1. D is the dialyzing cell, a cylinder of pyrex 9 cm. in diameter and 13 cm. in length with a hole H at the top. Over the flanged ends of the glass cylinder are stretched pieces of rubber tubing, such as may be used on Gooch crucibles. After these are given a light coating of vaseline, wet parchment papers are stretched over the ends and are tightly secured by means of long strings of rubber bands looped together somewhat like links in a chain. Against each of the membranes are placed six sheets of filter paper (Whatman No. 44, ash content 0.000120 gr.). These are cut to a point at the bottom. The tops are folded over for about 2 cm. and V-shaped holes are cut in the folded edges.

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* Contribution from Severance Chemical Laboratory of Oberlin College.

** The authors are indebted to Mr. Elton S. Cook for some of the quantitative measurements.

The electrodes E are cleaned carbon plates 13 cm. × 13 cm. × 6 mm. These are pressed lightly against the filter papers by means of ring clamps containing rubber stoppers, the clamps being supported by a rod fastened to a ring-stand (not shown in the figure). Distilled water from a 40-liter carboy is led through the tube Y, its rate of flow being regulated by the screw-clamps S, and is allowed to drop through the tubes T, which are drawn to capillary tips, into the V-holes of the filter paper F. This device guarantees the maintenance of a moving film of water the thickness of the filter papers. The electrodes must not be pressed too tightly or the water will tend to go around the ends of the dialyzer. The folding of the filter papers, giving greater thickness at the top, also helps to prevent this. The dialysate drops into the funnels G and is carried to the sink. Through the hole H is led a tube B carrying a stream of CO_2-free air which acts as a stirrer, although some other mechanical stirrer may be used at H. A heating coil C, enclosed in a pyrex tube, may be suspended through H if desired. The electrical connections are self-explanatory, A being an ammeter, V a voltmeter, P a single-pole double-throw switch, R and R′ variable resistances. For greater constancy of temperature, the whole apparatus, exclusive of the electrical instruments, is placed in a glass case.

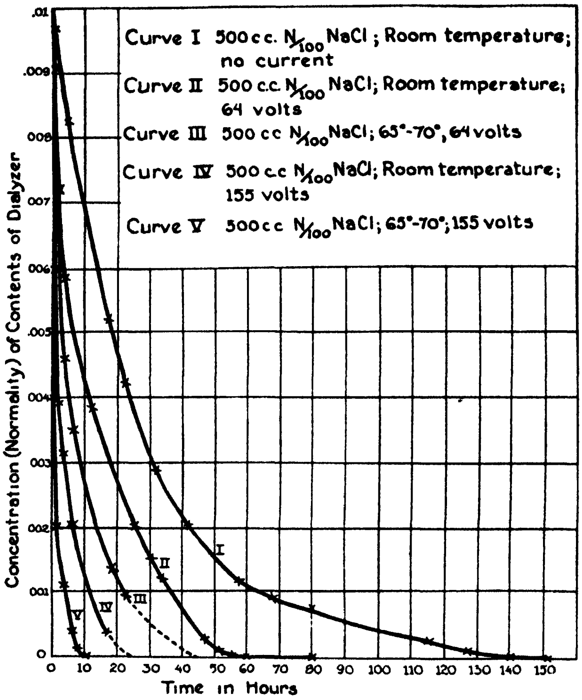

FIG. 2

Experimental

The results obtained with the apparatus are plotted in Figs. 2 and 3. In all determinations the source of current was storage batteries or storage batteries in series with B-batteries. The rate of flow of water over each electrode averaged 15 cc. per minute. Fig. 2, in which concentration of the solution in the dialyzer is plotted against time in hours, shows the removal of sodium and chlorine ions from N/100 NaCl. In each case 500 cc. of the solution was used. Concentration of the solution in the dialyzer was determined by titrating 5 cc. samples with N/100 silver nitrate, using saturated potassium dichromate as the indicator. The legend accompanying the figure explains the curves. It will be seen that, using 155 volts and maintaining the temperature at 55°-60°, no qualitative test for chloride ions could be obtained after 10 hours, while at room temperature and with no current flowing over 150 hours were required for such effective removal of chloride ions.

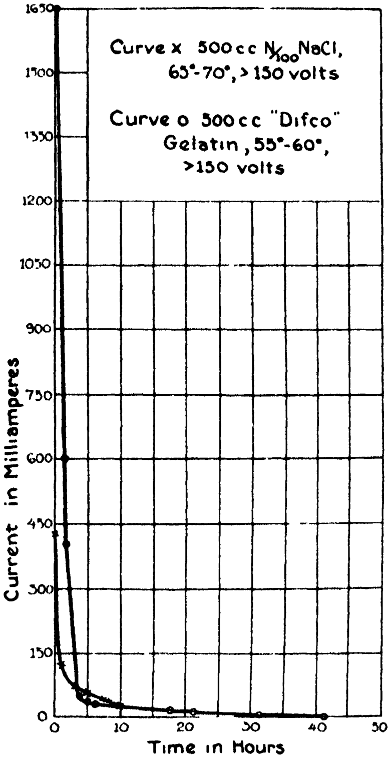

FIG. 3

Fig. 3, giving the results of dialyzing 500 cc. of 6% "Difco" gelatin at 155 volts and 55°-60°. A curve for N/100 NaCl, is included for comparison. In these curves, current in milliamperes is plotted against time in hours. The rapid drop of current during the first four hours of gelatin dialysis will be noted. The gelatin at this point still gave a test for sulfates. To remove this last trace of sulfate ion it was necessary to continue the dialysis in excess of 40 hours.

Experiments were carried out using N/100 HCl. At high voltages and high temparatures it was found that the membranes were attacked with consequent leakage.

The removal of adsorbed chloride ions from silica gel which had been treated with HCl to dissolve out the iron was also tried. This could be accomplished satisfactorily but not in so short a time as by continuous washing with warm water.

Some experiments were tried using platinum electrodes consisting of pieces of fairly coarse gauze, 2.5 cm × 3 cm., backed with glass plates.

The dialysis was not as efficient as with carbon electrodes. However, for the results to be comparable, platinum electrodes of larger dimensions should be used.

Heating the cell with a flame is not quite so good as heating with a resistance coil. Dialysis at 65°-70° is, of course, more effective because ionic movements are more rapid than at room temperatures.

Summary

1. A new, inexpensive and efficient cell for electrodialysis has been described.

2. It has been proved that, using N/100 NaCl, no test for chloride ions can be obtained after 10 hours of dialysis at 155 volts and 65°-70°.

3. The application of the cell to the removal of salts from gelatin has been shown.

PHOTOMICROGRAPHIC STUDIES OF SUCROSE CRYSTALS*

BY SYBIL WOODRUFF AND HELEN VAN GILDER

Introduction

Photomicrographs of fondants make it possible to compare the magnitude of crystals forming in syrups of varying composition. The sucrose crystals present in a fondant type of candy of good quality are of such small size that they cannot be felt by the tongue as distinct particles. A high-grade product is said to be "creamy" or smooth in texture when it is entirely free from the grit of detectable crystals. It is rather surprising that the tongue and roof of the mouth give a tactile response to particles so slightly greater in size as are those of perceptibly coarse fondant compared with the crystals of a finely-textured one. The measurements of crystals accompanying these photomicrographic records show that in two fondants which would be rated as fine and slightly gritty respectively, we are able to sense a difference in crystal dimension of but 6 or 10 microns.

The factors which determine the size of crystals developing in a syrup are then of considerable importance if a difference in size of about 10 microns between two samples represents the difference between a candy of poor and one of good texture. Besides these crystals of maximum size in a fondant there are many others barely visible at a magnification of 360 times and furthermore there are assuredly present still others of colloidal dimensions. The dispersion of these minute crystals of sucrose in a continuous phase of concentrated sugar syrup produces a product which is plastic and one whose consistency depends very largely upon the ratio existing between the two phases, and, therefore, in turn upon the composition of the syrup-phase. Since the presence of other sugars increases the solubility of the sucrose, the relative amount of syrup will be greater and the consistency of the fondant softer and more pliable the greater the amount present of sugar other than sucrose.

The size to which sucrose crystals will grow as the mass of candy "grains out" depends upon physical conditions as well as upon the composition of the syrup. Cooling the syrup to a highly supersaturated state before agitation is permitted, favors crystallization at countless points simultaneously and thereby reduces the opportunity for crystal nuclei to build up to great size. A syrup may contain such a proportion of invert sugar to sucrose that crystals of small size would be expected to form but, due to faulty manipulation, opportunity may be given for the particles to grow to a size exceeding that found in an acceptable product. Examples of manipulative errors which might so hinder the desired graining of sucrose are failure to continue agitating the syrup until crystallization is complete, the accidental seeding of the hot syrup, or the cooling of the syrup in a vessel with rough surfaces. Thus syrups containing even 15 percent reducing sugars can form coarse-grained candies under circumstances such as these; on the other hand, fondants of surprisingly fine texture and plasticity can be obtained when no reducing sugar at all is present, providing the physical conditions for crystallization are cleverly controlled.

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The only other published photomicrographs of fondants are those by Halliday and Noble,[1] which illustrate only the differences caused by manipulative procedure and not those of different syrup composition. The photomicrographs of our study illustrate the effect upon the size of sucrose crystals of varying amounts of invert sugar produced by boiling sucrose in turn with hydrochloric, tartaric and citric acids, and with acid potassium tartrate; also the action of added glucose or fructose with reference to maximal crystal size. Measurements of the largest and smallest crystals in the micrographic fields have been made in freshly made fondant and in that which had been stored for some time. Variations in the physical conditions attending crystallization were avoided as perfectly as possible.

Experimental Methods

Preparation of fondant. One volume of sugar to one-half volume of water, or 200 grams of commercial sucrose to 118 grams of distilled water, were boiled together in a beaker. A sugar solution of this concentration had a boiling temperature of approximately 103°C and the rate of boiling was always so adjusted that the syrup reached the desired concentration and a boiling temperature of 115° in 20 minutes. Analysis showed about 30 grams of the original 118 grams of water to remain in the final fondant. Such an excess of water at the start was necessary since if much less than this was used there appeared to be an incomplete dissolving of the sucrose, thus making it less possible to control its recrystallization. The syrup boiled to 115° was therefore supersaturated as soon as it began to cool and if permitted to cool to 40° before any nuclei of granulation appeared, agitation produced crystals of small size. The hot syrup was poured immediately into a shallow glass bowl, allowed to cool undisturbed to 40°, then was beaten with a wooden spoon until it had changed to a plastic mass. It was kneaded smooth and stored in air-tight jars.

The procedure was the same when acid was boiled with the sugar and also when other sugars were substituted for a part of the sucrose. It had been found by a preliminary test that 0.2 grams of potassium acid tartrate to 200 grams of sugar which is an amount frequently called for in the home-made article, gave a product of satisfactory grain and contained 7.5 percent of invert sugar on the basis of the moist fondant. Therefore, in substituting glucose or fructose for part of the sucrose, such an amount of each was used as would give this quantity of reducing sugar in the fondant.

Photomicrographic Technique. The chief difficulty in mounting the specimen for microscopic observation was in spreading the fondant on the slide in a sufficiently thin smear. A very small amount of the fondant from the center of the jar was transferred to a drop of Canada balsam on the slide, a cover slip was pressed down upon it and moved to and fro between the thumb and forefinger until a thin layer of the specimen was obtained. A photomicrograph was made using a Leitz "Makam" camera and a magnification of 360 times. It was found that ordinary light with a ground-glass shield over the source, gave a better negative than did polarized light; also that a six-minute exposure under these circumstances was satisfactory. When samples were to be photographed after they had been stored, fresh smears from the center of the jar were prepared.

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[1] Halliday and Noble: "The Hows and Whys of Cooking," p. 139 (1928).

Determination of hydrogen ion concentration. This measurement was made with a Leeds and Northrup quinhydrone electrode at 25°C upon solutions containing 10 grams of fondant in 50 cc. The freshly boiled, distilled water used in making the dilutions had a pH of 5.83.

Determination of reducing sugar. The method used was the iodine titration modification of the well-known Munson and Walker one. The accuracy of the method for the case in hand was determined by checking the reducing sugar content of known combinations of sucrose with glucose or fructose or mixtures of the two wherein the reducing sugar varied from 7 to 30 percent of the total sugar present. The maximum deviation from the expected result was but 5 percent of the reducing sugar known to have been added. In a fondant containing, as it well may, 10 percent of its moist weight in the form of invert sugar or glucose, an error of 5 percent in the analysis of invert sugar would raise or lower the expected percent of invert sugar in the fondant to but 10.5 or 9.5. The characteristics of fondants do not change rapidly with small variations in the percent of invert sugar present; hence, it is believed that the accuracy obtainable with this method is sufficient for the purpose.

Discussion of Results

Invert Sugar produced by Different Acids. The inverting effect of acids or acid salts other than potassium acid tartrate (cream of tartar) has not been studied in connection with candy making. A paper by Carrick[2] gave 6.28 as the percent of invert sugar formed by boiling for 15 minutes a sugar solution consisting of 210 grams of sucrose and 0.3 grams of cream of tartar; this quantity of invert sugar was said to have given a desirable plasticity to the fondant. Daniels and Cook[3] have reported the invert sugar in a series of fondants containing from none to 1.2 grams of cream of tartar used with 110 grams of sugar and alkaline tap water. Their report did not describe the textures of the resulting candies, however.

Before the days of commercial glucose fondant was made by boiling the syrup with a small amount of "cream of tartar" and many rules for making the candy still suggest the use of acid. A study of this means of controlling crystal size was undertaken in a series of three fondants containing in turn

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[2] Carrick: J. Phys. Chem., 23, 589 (1919).

[3] Daniels and Cook: J Home Econ., 11, 65 (1919).

0.2 gram (an amount frequently recommended), 0.4 and 0.8 grams of potassium acid tartrate to 200 grams of sugar which served as a means of showing what effect the correspondingly increasing amount of invert sugar would have upon the size attained by the sucrose crystals. It had been expected that when citric, tartaric and hydrochloric acids were used in such amounts as to give the same hydrogen ion concentration as that shown by the "cream of tartar" samples, the same amounts of invert sugar would likewise be produced during boiling and therefore similar effects upon the crystallization of the sucrose. The actual results as they are recorded in Table I do not show this to be the case, however.

TABLE I

Amounts of invert sugar and pH of fondants containing various acids (Percent based upon moist fondant)

Sample Number	Acid		pH of Fondant Average	Average Invert Sugar Percent
	Kind	Amount Milligrams		
1 b	None		5.33	0.42
4 a	K-H-tartrate	200	4.10	6.49
b	" " "	400	3.82	11.10
c	" " "	800	3.73	15.80
5 a	Citric acid	10	4.72	7.00
b	" "	20	4.20	16.30‡
c	" "	40	3.85	43.43*
6 a	Tartaric acid	10	4.37	13.05
b	" "	20	4.02	23.55‡
7 a	Hydrochloric acid	46 cc.	4.86	6.35
b	" "	69 cc.	4.37	above 50.00*

Note: The period of boiling to a temperature of 115°C. was 20 minutes in each fondant. All syrups were cooled to 40°C. before crsytallization was induced. The amounts of acid are for 200 grams of sucrose. The HCl was 0.001 N.

* Syrup did not crystallize.

‡ Syrup crystallized after 50 to 60 minutes of beating whereas others grained in from 7 to 15 minutes.

There was so little relation between the manner and completeness with which sucrose crystallized from the syrup and the pH of the solution that it seemed as feasible a way as any to record results given by 10, 20, and 40 mg. of citric acid, by 10 and 20 mg. of tartaric, and by 46 and 69 cc. of 0.001 N hydrochloric acid. The citric acid and hydrochloric acid fondants contained about 7 percent of invert sugar each, for instance, when their pH was but 4.72 and 4.86 respectively. This was approximately the same amount of invert sugar as that contained in the product carrying 200 mg. K-H-tartrate and pH 4.10. The pH produced by 800 mg. of K-H-tartrate was 3.73 but the invert sugar formed was nevertheless 15.80 percent; contrast this with the 43.43 percent invert sugar induced by a pH of 3.85 with 40 mg. of citric, 23.55 percent by 20 mg. of tartaric (pH 4.02) and more than 50 percent by such an amount of HCl as gave pH 4.37. Neither was there as marked a taste of sourness in citric and hydrochloric acid fondants as there was in that containing 800 mg. of K-H-tartrate even where the three were similar in degree of softness.

As for consistency and ease of molding, the syrups containing 43.43 percent or more invert sugar would not deposit any sucrose crystals even with long beating and long standing. One containing 23.55 percent crystallized to a semi-fluid mass after 60 minutes of continuous beating; one with 16.30 percent crystallized to a very soft product after 50 minutes of beating and one of 15.80 percent invert sugar was plastic but too soft to be molded easily. The 6 to 7 percent of invert sugar always gave a firm, moldable fondant free from detectable "grits" of large crystals. It would appear therefore that from 6 to 15 percent invert sugar for a fondant containing 13 percent moisture, represents the limits of possibilities for convenient molding, the lower figure giving a firm, moldable product and the upper one a softer and still more finely grained candy.

Effect of glucose and fructose upon texture. It has been shown that the invert sugar content of fondant must be kept within the limits of approximately 6 to 15 percent for superior texture and ease of molding. It is not a simple matter so to regulate conditions that this percent can be attained. It is far less complicated as a procedure to add the desired amount of glucose or some other simple sugar at the beginning than to depend upon the formation of invert sugar, the amount of which will be uncertain unless the length of the boiling period and the kind and amount of acid are all under control.

Glucose has commonly been used in the making of a fondant type of candy but usually in the form of corn syrup which contains along with glucose, dextrins and maltose. It seemed desirable to know whether pure glucose used in the same percentage as the invert sugar of the preceding part of the study would control crystal size in the same manner. Fructose was also used in a similar manner. Each sugar, in amounts to correspond to approximately 7.46 percent of reducing sugar in the moist fondant, was boiled with sucrose and water and crystallization induced in the usual fashion. Each gave a product smooth to the tongue and firmly moldable, not showing any of the stickiness upon which the invert sugar products bordered when they were equally fine in texture. The fructose, the purest obtainable, imparted a caramel-like flavor and a visible color to the candy, however.

The moisture content of fondant. The results thus far refer, where softness and plasticity are concerned, to a fondant whose syrup was boiled to a temperature of 115°C. A product, concentrated to this degree and made with no inverting agent or glucose, was found by analysis to contain 13.07 percent (average) moisture. The percents of moisture found for boiling temperatures of 113° and 117° were 15.73 and 11.59 respectively. This shows that a difference of one degree downward from 115° alters the moisture in the fondant by 3 grams per 200 grams of sugar; this much extra water made the consistency markedly softer. The moisture content of fondants containing invert sugar or glucose and boiled to 115° was not significantly different from the figures obtained for plain water fondant. These determinations of moisture were made by drying 2 gram samples, spread out upon the bottom of a shallow, wide, weighing bottle, uncovered during drying in vacuo at 56° to 60°C. for approximately 8 hours. The cover of the weighing bottle was in place during all weighing operations to prevent the hygroscopic material from changing weight.

Photomicrographs and sucrose crystal size. Photomicrographs were made of all the fondants previously described. The average diagonal measurement of six of the largest and of six of the smallest crystals in each microscopic field has been recorded in Table II. The millimeters of length of the crystals at a magnification of 360 times were reduced to microns of actual size; the method of measurement, though crude, gave comparative results of significance.

A micrograph has been included (Plate 1), showing the contrastingly large size of crystals attained in an admittedly coarse product wherein the syrup was beaten at 70°C. and opportunity given for the crystals to grow to large proportions. Plates II to XII inclusive are photomicrographs of the fondants of the composition given in Table II.

TABLE II

Approximate size of sucrose crystals shown in photomicrographs of fondants containing invert sugar and other reducing sugars

		Acid or Reducing Sugar Added			Crystal Diagonal Lengths	
Sample Number	Plate Number	Kind	Weight[†] Milligrams	Reducing Sugar Percent	Smallest Microns	Largest Microns
1 a[*]	I	None		—	7.0	45.5
b	II	None		0.42	5.0	25.5
2	III	Glucose		7.46	3.8	19.6
3	IV	Fructose		7.46	3.8	15.2
4 a	V	K-H-tartrate	200	6.49	5.2	15.5
b	VI	K-H-tartrate	400	11.10	3.6	12.5
c	VII	K-H-tartrate	800	15.80	2.8	13.2
5 a	VIII	Citric Acid	10	7.00	3.3	18.8
b	IX	Cirtic Acid	20	16.30	2.7	10.0
6 a	X	Tartaric Acid	10	13.05	3.0	11.3
b	XI	Tartaric Acid	20	23.55	2.7	11.1
7 a	XII	Hydrochloric Acid	46 cc.[‡]	6.35	3.1	12.2

[†] Milligrams per 200 grams of sucrose.

[*] Beaten while syrup was at a temperature of 70°C. All others in the table were beaten at a temperature of 40°C.

[‡] Refers to 0.001N solution.

All the fondants of the series, with the exception of the one made with water alone, were smooth and fine in texture, those containing large percentages of invert sugar being so very fine that they were like soft putty in feel and so plastic that they could be stretched. The ones containing less invert sugar were free from grittiness but were of more solid consistency, and

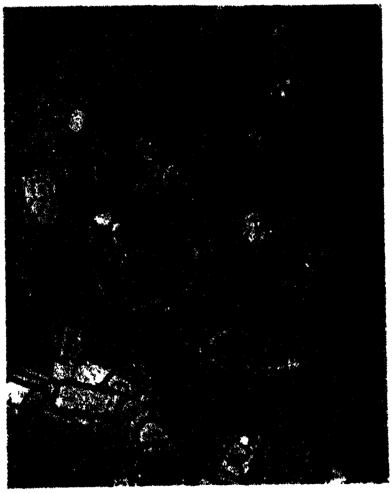


PLATE I.
Photomicrograph of fondant no. 1a. Crystals of this size make a coarse texture Syrup was beaten hot.

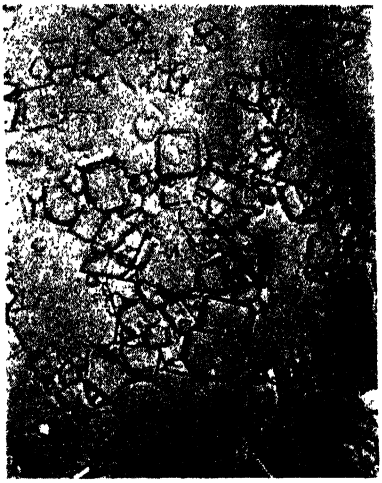


PLATE II.
Photomicrograph of fondant no. 1b. Texture was good except for occasional "grits." Syrup was beaten cold.

PLATE III.
Photomicrograph of fondant no. 2, containing glucose.

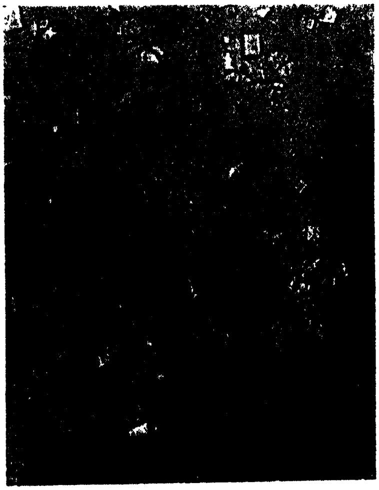


PLATE IV.
Photomicrograph of fondant no. 3, containing fructose.

Magnification X 360

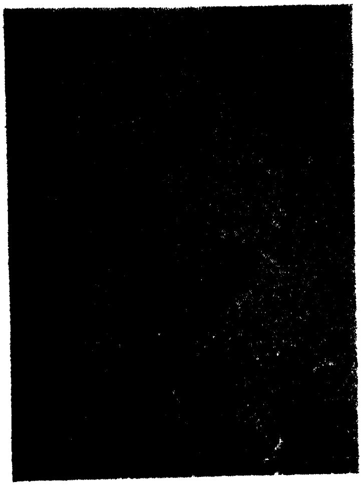


PLATE V.
Photomicrograph of fondant no. 4a, containing 200 mg. of potassium acid tartrate.

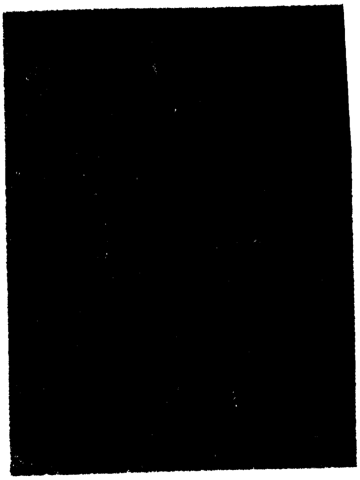


PLATE VI.
Photomicrograph of fondant no. 4b, containing 400 mg. of potassium acid tartrate.

PLATE VII.
Photomicrograph of fondant no. 4c, containing 800 mg. of potassium acid tartrate.

PLATE VIII.
Photomocrograph of fondant no. 5a, containing 10 mg. of citric acid.

Magnification X 360

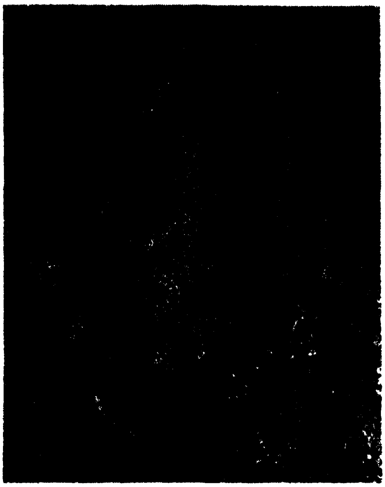


PLATE IX.
Photomicrograph of fondant no. 5b, containing 20 mg. of citric acid.

PLATE X.
Photomicrograph of fondant no. 6a, containing 10 mg. of tartaric acid.

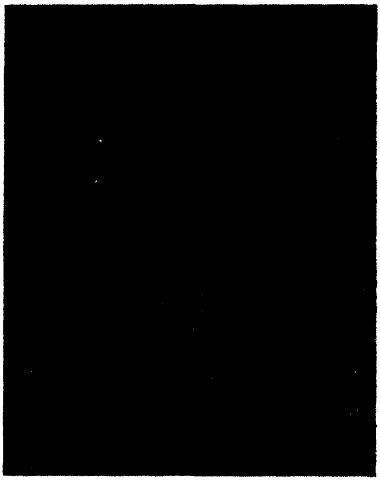


PLATE XI.
Photomicrograph of fondant no. 6b, containing 20 mg. of tartaric acid.

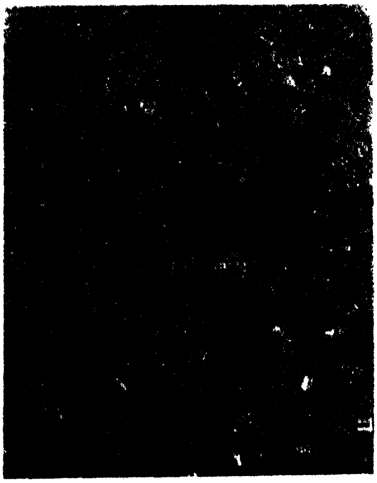


PLATE XII
Photomicrograph of fondant no. 7a, containing 46 cc. of 0.001N HCl.

Magnification × 360

broke apart when pulled. The fondant made with water alone looked and felt much like those which contained small amounts of invert sugar; but when it was chewed there were noticed occasional grits of either large single crystals or possibly of crystal clusters. An indiscriminating person would have pronounced this a good product and it was, to be sure, superior to many of the home-made candies of questionable quality which are consumed with apparent relish.

It will be noted that there were some crystals but 7μ across even in the coarse fondant, number 1a, though the maximum size attained by them was many times that. There was little variation in the size of the smallest crystals in the different fondants, indicating probably that 3μ approached the limits of visibility. It is conceivable that there were present many crystals which could not be seen even at a magnification of 360 times. The largest crystals in the coarse candy (1a) measured 45.5μ across; the largest ones in number 1b, which also contained no invert sugar but whose syrup was beaten after it had cooled to 40°, were 25.5μ in size. Two other samples, numbers 2 and 5a showed crystals not much smaller than those of 1b, but even though their largest crystals measured 19.6 and 18.8μ there were no grits discernible when the fondants were chewed. This must mean that in a product like this the ability to note particle size by the sense of touch in the mouth, ceases with dimensions which lie some place between 19.5 and 25.5μ. The crystals of all other samples were at least 10μ smaller than the 25.5μ size of the gritty ones. Reducing sugar in quantities of 6.49 to 7.46 percent permitted crystals to grow to a somewhat larger size, 15.2 to 19.6μ, than did 11.10 percent or more invert sugar, in the presence of which the maximum crystals measured but 10.0 to 13.2μ. The odd member of the series was the hydrochloric acid fondant containing but 6.35 percent invert sugar and yet crystals only 12.2μ in length. The crystals of this sample also appeared misshapen and indistinct in outline in comparison with others.

The results show that when the same amounts of each invert sugar, glucose and fructose are present they are equally effective as a means of regulating crystal size. For ease and certainty, the use of known quantities of glucose or fructose is preferred to partial inversion during boiling. The inverting agent may just as well be either potassium acid tartrate or citric or tartaric acids though the two acids act so powerfully in comparison with the acid salt that it is easy to understand the preference for the latter in recipes calling for roughly measured ingredients. It was still less easily possible to limit and control inversion by hydrochloric acid than it was by citric and tartaric.

The size of the largest crystals in the photomicrographic field was roughly inversely proportional to the amount of invert sugar though never less than 10 to 12 microns regardless of the percent of invert sugar present. There was no means of estimating accurately the relative numbers of small and large crystals in products of different composition. There appears to be no point, therefore, in seeking to have larger amounts of invert sugar than about 16 percent for the purpose of keeping the crystals small; more invert sugar

PLATE XIII.

Photomicrograph of fondant no. 1b after stored 7 days. Compare with Plates II and XIV.

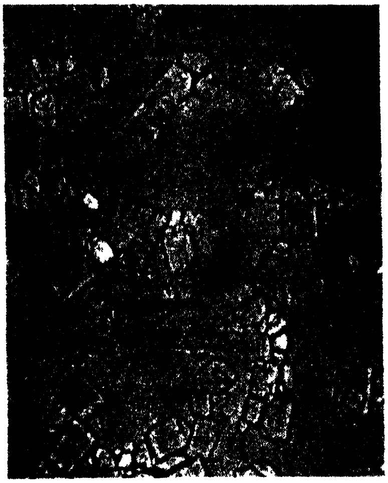
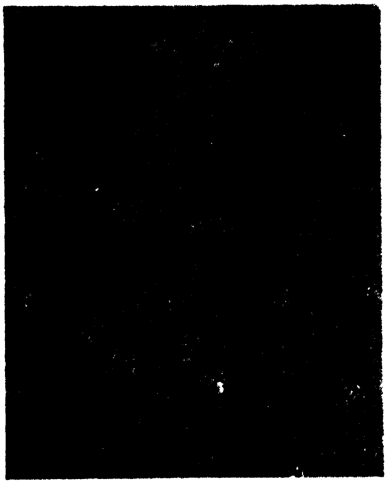


PLATE XIV.

Photomicrograph of fondant no. 1b, after stored 21 days. Compare with Plates II and XIII.



PLATES XV.

Photomicrograph of fondant no. 4b (400 mg. K-H-tartrate), after stored 7 days. Compare with Plates VI and XVI.

PLATE XVI.

Photomicrograph of fondant no. 4b (400 mg. K-H-tartrate), after stored 21 days. Compare with Plates VI and XV.

Magnification × 360

may act favorably in another direction by increasing the ratio of syrup phase to solid phase and thus enhancing the flowing quality of the cream candy.

Crystal size after storage. It is a common observation that fondants do not tend to become coarser in texture as they age but rather that they ripen to an even smoother and more uniform grain. It is, therefore, of interest to see what alterations occur in microscopic appearance and crystal dimension. The fondants photographed in plates II to XII were afterward all stored for a period of at least 7 days after which new micrographs were made. The sample made with no inverting agent and those made with potassium acid tartrate were photographed again after 21 days of storing. Characteristically the same results were obtained in all cases; therefore, only the photomicrographs of the samples containing none and 400 milligrams of K-H-tartrate and stored for 7 and 21 days are shown in plates XIII to XVI inclusive. The numerical measurements of the smallest and the largest crystals at 1, 7 and 21 days are to be found in Table III.

TABLE III

Approximate size of sucrose crystals in fondants with and without K-H-tartrate after 7 and 21 days of storage (Size in microns)

Sample Number	K-H-tartrate Milligrams	Average Diagonal Length of Sucrose Crystals					
		Smallest			Largest		
		1st Day	7th Day	21st Day	1st Day	7th Day	21st Day
1 b*	None	5.0	5.8	6.1	25.5	28.3	26.1
4 a	200	5.2	5.2	6.1	15.5	18.3	20.0
b‡	400	3.6	4.0	3.3	12.5	13.3	14.4
c	800	2.8	3.3	2.8	13.2	15.8	17.5

* See Plates II, XIII and XIV for 1, 7 and 21 days, respectively.
‡ See plates VI, XV and XVI for 1, 7 and 21 days, respectively.

No change in crystal size is casually apparent in the micrographs; any change in the small crystals comes well within the limits of error of measurement. This is more or less true of the largest crystals in the field; the increases found were never more than 4.5μ and usually were even less than this. Therefore, the size of the grains at the time the candy is first made will determine almost entirely their size after the candy becomes several weeks old.

This interpretation of the significance of the change in size of sucrose crystals is different from that given by Halliday and Noble who report a growth of crystals during storage without indicating any actual measurements. Their comment implies to the average reader an increase sufficiently great to alter the character of the grain of the fondant. That this is unlikely is indicated by the measurements given in our report.

Summary

Photomicrographs have been shown of masses of sucrose crystals in fondants containing glucose, fructose and varying amounts of invert sugar. The average diagonal measurements of the largest and the smallest crystals in the micrographic fields have been reported in microns.

Glucose, fructose and invert sugar served equally well in regulating the size of crystals. It was far from easy, however, so to adjust the conditions that the amount of invert sugar arising could be predicted. Inversion was so rapid as to make its control difficult when citric, tartaric or hydrochloric acids were used, though potassium acid tartrate was far slower even at the same pH. Under the conditions of the experiment, no exact relationship between the pH of the syrup and the amount of inversion was noted when different kinds of acids were used.

Syrups containing 43.43 percent or more invert sugar would not crystallize; those containing 16.30 to 23.55 percent formed a semi-fluid mass of crystals. From 6 to 15.80 percent invert sugar permitted a satisfactory proportion of the sucrose to crystallize out to give a plastic, moldable product.

In the presence of 11.10 percent or more invert sugar the crystals of maximum size measured 10.0 to 13.2 microns and the grain was exceedingly fine. Fondants containing about 7 percent reducing sugar of either kind were of agreeably fine texture and in them the largest crystals were 15 to 19 microns across. Candy observed to be coarse in texture contained crystals 45 microns in size. The crystals of all these samples were found not to grow noticeably in dimensions when the fondants were stored for 7 to 21 days.

The sense of touch in the mouth can detect a difference of about 6 to 10 microns in size of crystals as representing the difference between a smooth and a "gritty" texture.

THE MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES. II. HYDROUS ALUMINA SOLS

BY HARRY B. WEISER

In a paper presented before the Eighth Colloid Symposium[1] an adsorption mechanism was outlined to account for the change in composition and nature of the double layer which results in a decrease in the charge on the micelle when electrolytes are added to hydrous oxide sols. The proposed mechanism was the outgrowth of potentiometric observations of the change in chloride ion concentration during the stepwise addition of electrolytes to hydrous ferric oxide sol containing a slight excess of hydrochloric acid or ferric chloride as stabilizing electrolyte. At the same Symposium, Thomas and Whitehead[2] reported on their observations of the change in hydrogen ion activity when electrolytes were added to hydrous alumina sol formed by peptizing precipitated alumina with the minimum amount of hydrochloric acid to ensure stability and centrifuging to remove any unpeptized oxide. Under the condition of their observations, it was found that the pH value of the sol was increased by the addition of approximately neutral electrolytes, the anion order being oxalate > acetate > sulfate > halides > nitrate. To explain the observed increase in pH value Thomas and Whitehead assumed that the alumina sols are Werner complexes resembling the poly-ol basic chromic salts formulated by Bjerrum.[3] Starting with this postulate the increase in pH value on adding salts was attributed to replacement of (OH) groups by the anion of the added salt, followed by the union of the displaced OH radicals with hydrogen ion to form water. The pH value of the sols peptized by HCl was found to increase slightly on standing at room temperature, but on subsequent heating the pH value decreased and the change was irreversible.

In the absence of any independent proof of the constitution of the alumina sols proposed by Thomas and Whitehead, the hypothesis can be regarded only as a suggestive qualitative one for the present. Certainly if alumina sols behave like ferric oxide sols in the presence of electrolytes, the picture will have to be modified to account for the observed fact that chloride ion rather than hydroxyl ion appears to be largely displaced by the added anions.

Although the action of salts on colloidal alumina is not considered by Thomas and Whitehead in its bearing on the coagulation of sols, it is evident from observations with colloidal ferric oxide that the stepwise addition of electrolytes below the precipitation value is accompanied by a gradual decrease in micellar charge with a consequent increase in the tendency of the micelles to agglomerate into larger aggregates. The change in specific surface accompanying this phenomenon has a marked effect on the adsorption equilibria. This manifests itself in the form of the chloride displacement curve on adding electrolytes and one should expect it to influence the pH value of the sol.

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[1] Weiser: J. Phys. Chem., 35, 1 (1931).

[2] J. Phys. Chem., 35, 27 (1931).

[3] Z. physik. Chem., 59, 336 (1907); 73, 724 (1910).

The decrease in the pH value of alumina sols on heating and their failure to return to the original value on cooling are likewise explained by Thomas and Whitehead by using the postulates of Bjerrum[1] and Stiasny,[2] namely, that aquo groups in the complex radical give up $H^{\cdot}$ ions leaving hydroxo groups which then become "olated" forming larger aggregates. These hypotheses do not take into account the well-known decrease in the hydrous character of the colloidal particles on heating and the accompanying change in the extent and nature of the surface of the particles which will markedly influence the adsorption equilibria. The ageing which takes place at ordinary temperatures manifests itself in a similar but much slower change in the surface of the particles. As will be pointed out later, we failed to observe an increase in pH value on ageing sols formed by peptization with $AlCl_3$.

In this paper will be given a report of observations on the change in the chloride ion concentration and in the pH value of alumina sols prepared by two different methods, when electrolytes are added to the sols above and below the precipitation value. In addition, the effect of ageing on the pH value of the different sols will be considered.

Preparation of Sols

(1) *Peptization of "Grown" Alumina.* A method was sought for the preparation of alumina sol by peptization of an alumina which was not formed by the hydrolysis of an aluminum salt. If such could be done there would seem to be no more reason for assuming that the alumina sol is a complex Werner compound of indefinite composition than for assuming that silver halide sols formed by peptization with a slight excess of silver nitrate[3] are complex subhalides of indefinite composition. A method for preparing the alumina sol by peptization of pure alumina was suggested by an earlier observation[4] that "grown" alumina[5] formed by the activation of amalgamated aluminum on water was held in the colloidal state by a trace of HCl. The method of procedure finally worked out for the preparation of the sol was as follows: After burnishing to remove the film of oxide from sheets of aluminum 10 cm x 20 cm in size, they were placed in dilute hydrochloric acid which was allowed to act until the surface was thoroughly cleaned. Following this, they were rinsed and dropped immediately into a solution of mercuric chloride. After a minute the sheets were taken out, washed thoroughly to remove the loose film of mercury, rinsed with distilled water, and each one placed in a liter of approximately 0.015 normal $AlCl_3$ which was stirred continuously

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[1] Loc. cit.

[2] Stiasny and Grimm: Collegium, **691**, 505 (1907); Stiasny and Szego: **670**, 41 (1926).

[3] Lottermoser: J. prakt. Chem., (2) **72**, 39 (1905).

[4] Weiser: J. Phys. Chem., **33**, 1713 (1929); Cf. also, Pauli and Schmidt: Z. physik. Chem., **129**, 199 (1927).

[5] Wislicenus: Kolloid-Z., 2nd Supplement XI (1908).

with a mechanical stirrer. The action was quite rapid at the start as evidenced by the rate of evolution of hydrogen. The "grown" alumina which was formed was held in the sol state owing to preferential adsorption of aluminum and hydrogen ions. After several hours the action slowed down and the metal was re-treated as previously described. The process was continued until a sol of the desired composition was obtained or until no more of the "grown" alumina was peptized even when a large excess of unpeptized oxide was present. Sol I used in preliminary observations still contained a little unadsorbed aluminum ion and so would have peptized more alumina. Sol II, on the other hand, was almost free from unadsorbed aluminum ion.

(2) *Hydrolysis of Aluminum Chloride.* For the purpose of comparison, a third sol was prepared by the usual method of hydrolysis of $AlCl_3$ followed by dialysis. To a liter of solution containing approximately 100 grams of $AlCl_3.6H_2O$ was added ammonia slowly until the precipitate which was formed just failed to be peptized completely. The mixture was diluted to 3.5 liters and was boiled for 30 minutes after which it was dialyzed at the boiling point in Neidle[1] dialyzers through which water was allowed to flow continuously. The process was continued until an analysis showed a suitable ratio of alumina to chlorine and the sol was then concentrated by evaporation to the desired composition.

The sols were analyzed for alumina content by precipitating with a slight excess of ammonia, washing, igniting, and weighing in the usual manner. The chloride content was determined by adding to a 25 cc portion of sol, an amount of $AgNO_3$ which was found by a preliminary experiment to be slightly in excess of that necessary to react with all the chloride. Nitric acid was then added and the mixture digested on the hot plate in the dark until all the oxide was dissolved. After diluting, the silver salt was collected on a Gooch crucible, dried and weighed. The composition of the three sols is given in the following table.

Composition of Alumina Sols

Sol No.	Method of Preparation	Al_2O_3 grams per liter	Cl mols per liter
I	Peptization of "grown" Al_2O_3	3.01	0.0160
II	Peptization of "grown" Al_2O_3	4.12	0.0156
III	$AlCl_3$ treated with NH_4OH short of precipitation and dialyzed	4.10	0.0164

In order to obviate any marked change in the composition of the sols during the course of the observations on them, they were allowed to age from two to three weeks before using.

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[1] J. Am. Chem. Soc., 38, 1270 (1916).

Observations on Alumina Sol I

The change in chloride ion concentration during the stepwise addition of electrolytes to the sols was determined by the same procedure as given in detail in an earlier paper.[1] It consists essentially of mixing separate portions of sol with gradually increasing amounts of electrolytes making the observations on the separate samples. Twenty-cubic-centimeter portions of sol in which was suspended a small amount of pure calomel, were mixed with a definite volume of standard electrolyte diluted to 5 cc in a mixing apparatus dried each time before use. After transferring the mixture to a 30 cc weighing bottle which had been thoroughly cleaned and steamed, it was placed in a thermostat at 25° and shaken at intervals for 24 hours. It was then placed in the electrode vessel like that shown in Fig. 2 of the paper above mentioned and after standing 24 hours longer, the potential was measured against an $N/10$ calomel electrode. The potentiometer employed was the Leeds and Northrop Type K apparatus in conjunction with a Hartman and Braun moving coil galvanometer sensitive to 0.1 millivolt. From the observed potential the activity of the chloride as potassium chloride was calculated and from this the molar concentration was obtained by dividing by the corresponding activity coefficient as read off from a graph prepared from data given by Lewis and Randall.[2]

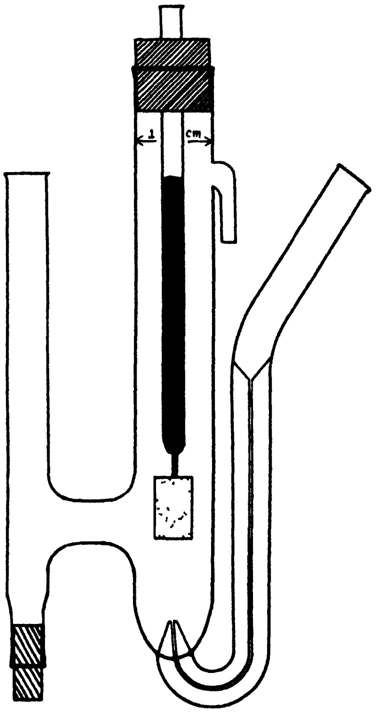

FIG. 1
Diagram of Hydrogen Electrode Vessel

Since the quinhydrone electrode gives erroneous values in unbuffered solutions with a pH value greater than 5,[3] the pH-value measurements were made with the hydrogen electrode in most cases. For this purpose the hydrogen electrode vessel of Pyrex designed by Dr. Everett E. Porter was found to be especially useful. The essential features of the vessel, shown in Fig. 1, are the hydrogen inlet device for giving small bubbles that stir the solution continuously and saturate it promptly; the small capacity, 4 or 5 cc being adequate test solution; the connecting bridge; and the outlet tube near the top through which is discharged the froth likely to form when a gas is bubbled through a sol. The electrodes were of platinized platinum foil 6 mm × 8 mm in size. The hydrogen from a tank was purified by passing over an incandescent tungsten filament, next over sticks of KOH, then bubbled through sulfuric acid, and finally through water.

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[1] Weiser: J. Phys. Chem., 35, 1 (1931).
[2] "Thermodynamics," 344 (1923).
[3] Best: J. Phys. Chem., 34, 1815 (1930).

The hydrogen electrode can not be used to determine the pH value in the presence of KNO_3. Fortunately in the experiments with this salt the pH value remained in the neighborhood of 5 and the quinhydrone electrode would be expected to give reliable results. A gold electrode as supplied by Leeds and Northrop was employed in the test solution.

The same potentiometer set-up used in making the chloride ion measurements was employed in determining the pH values.

Freshly boiled distilled water and salts of tested purity were used throughout. Sols and solutions were stored in Pyrex vessels.

Titration with K_2SO_4. Since 20 cc of sol was precipitated with less than 5 cc of $N/20$ K_2SO_4, this concentration of salt was used in the experiments. Above the precipitation value all the suspended calomel was carried down by the precipitated oxide. To make sure that the supernatant solution was saturated with calomel, a small amount of paste was added at the time the mixture was transferred to the electrode vessel. Following the determination of the chloride ion concentrations of the several mixtures, the pH value of each was measured. The experimental results are given in Table I and plotted in Fig. 2, the points being represented by dots.

TABLE I

Titration of Al_2O_3 Sol I with K_2SO_4

Cc $N/20$ K_2SO_4 to 20 cc sol. Total volume 25 cc	π volts	$\alpha Cl^- \times 10^3$	$[Cl] \times 10^3$	$[Cl]$ displaced $\times 10^3$	$\frac{1}{2}[SO_4]$ added $\times 10^3$	pH final
0.0	0.0658	6.12	6.50	0.0	0	4.31
0.5	0.0644	6.46	6.88	0.38	1	4.38
1.0	0.0634	6.71	7.15	0.65	2	4.42
1.5	0.0620	7.08	7.56	1.06	3	4.44
2.0	0.0608	7.43	7.94	1.44	4	4.46
2.5	0.0593	7.93	8.50	2.00	5	——
3.0	0.0570	8.61	9.26	2.76	6	4.47
3.50	0.0552	9.24	9.97	3.47	7	——
3.75	0.0545	9.49	10.25	3.75	7.5	——
4.00	0.0540	9.68	10.47	3.97	8	4.48
4.50	0.0530	10.07	10.90	4.40	9	——
5.00	0.0521	10.43	11.32	4.82	10	4.49

Titration with $K_2C_2O_4$. The same procedure described in the preceding paragraph was repeated with $N/20$ $K_2C_2O_4$ instead of K_2SO_4. The results given in Table II are plotted in Fig. 2, the points on the curves with this salt being represented with circles.

A glance at the form of the chloride displacement curves reveals the S-form which characterized similar curves using ferric oxide sols. As with the latter sols, the amount of chloride displaced is always less than the amount of sulfate or chloride added. Moreover, the total chloride concentration of the

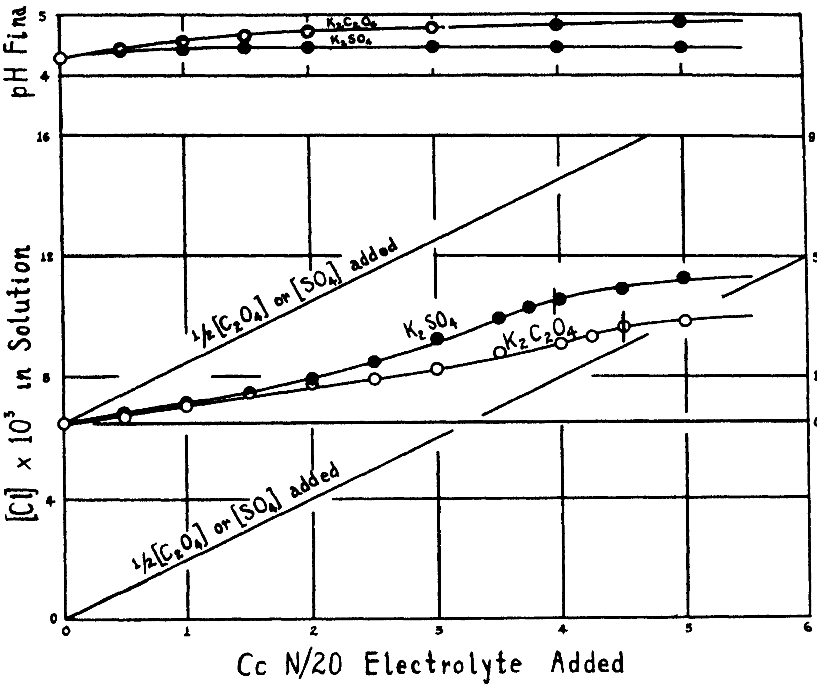

FIG. 2

Titration Curves for Al_2O_3 Sol I with $N/20$ K_2SO_4 and $N/20$ $K_2C_2O_4$

TABLE II

Titration of Al_2O_3 Sol I with $K_2C_2O_4$

Cc $N/20$ $K_2C_2O_4$ to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	$\frac{1}{2}$ [C_2O_4] added $\times 10^3$	pH final
0.0	0.0658	6.12	6.50	0 0	0	4.31
0.5	0.0646	6.41	6.82	0.32	1	4.43
1.0	0.0637	6.64	7.07	0.47	2	4.57
1.5	0.0620	7.08	7.56	1.06	3	4.67
2.0	0.0614	7.25	7.75	1.25	4	4.73
2.5	0.0608	7.43	7.94	1.44	5	——
3.0	0.0600	7.67	8.21	1.71	6	4.80
3.5	0.0583	8.22	8.82	2.32	7	——
4.0	0.0576	8.42	9.06	2.56	8	4.85
4.25	0.0571	8.59	9.24	2.74	8.5	——
4.5	0.0567	8.96	9.65	3.15	9	——
5.0	0.0556	9.10	9.81	3.31	10	4.91

solution at the precipitation value (shown by the vertical line cutting the curve) approximates the concentration of the added salts. The displacement of chloride by sulfate is greater at all concentrations than that of oxalate and the precipitation value of the former is the lower. This is usually true in fairly acid solution since in such cases there is a relatively higher concentration of univalent bioxalate ions than of univalent bisulfate; and in general, the bivalent ions are more strongly adsorbed and so have a more marked displacing power than univalent ions at the same concentration.

The pH values of the sol-sulfate mixtures were but very little more than that of the pure sol; with the sol-oxalate mixtures a somewhat greater increase was noted, as might be expected since solutions of $K_2C_2O_4$ are slightly alkaline.

Experiments with Alumina Sol II

The results of the preliminary experiments with Sol I were sufficiently promising that the investigations were continued with Sol II which was similar in total chloride content to Sol I but contained 35 percent more Al_2O_3. In the preliminary experiments, the mistake was made of using too low a concentration of electrolyte so that but little information was obtained above the precipitation value. With the stronger sol, $N/10$ solutions of the salts with multivalent anions were employed. Moreover, it seemed of value to know the pH value of the electrolytes alone at the same concentration as the sol-electrolyte mixture. Accordingly the pH values were determined for mixtures in which water was substituted for the sol. In the subsequent tables the pH values for sol-electrolyte mixtures and for the pure solutions are labeled respectively "pH final" and "pH initial."

Titration with K_2SO_4. The chloride displacement and pH values on adding $N/10$ K_3SO_4 in gradually increasing amounts to the sol are given in Table III and represented graphically in Fig. 3.

A comparison of the chloride displacement curve with that obtained with ferric oxide sol under similar conditions reveals a striking similarity in behavior. Note the usual upward course before the precipitation value is

TABLE III

Titration of Al_2O_3 Sol II with K_2SO_4

Cc $N/10$ K_2SO_4 to 20 cc sol. Total volume 25 cc.	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	½ [SO_4] added $\times 10^3$	pH final	initial
0.0	0.0635	6.78	7.21	0.9	0	4.20	—
0.5	0.0605	7.52	8.04	0.83	2	4.24	—
1.0	0.0581	8.25	8.85	1.64	4	4.25	7.33
1.5	0.0565	8.78	9.43	2.22	6	—	—
2.0	0.0535	9.87	10.68	3.47	8	4.26	7.43
2.5	0.0500	11.32	12.32	5.11	10	—	—
3.0	0.0485	12.00	13.10	5.89	12	4.32	7.56
4.0	0.0474	12.59	13.79	6.58	16	4.38	7.56
5.0	0.0470	12.72	13.93	6.72	20	4.43	7.56

reached. This is due to the gradual agglomeration of the particles and the consequent proportionately greater displacement of chloride for a given increment in sulfate concentration owing to decrease in the extent of surface. Note also that the curve changes direction in the immediate region of the precipitation value, the upper portion of the curve representing the relatively smaller displacement of chloride from the coagulum for a given increment in sulfate concentration. Again, the amount of chloride displaced is much smaller than the total sulfate added, but in the region of the precipitation value the total concentration is approximately equivalent to the sulfate added, although the variation from equivalence in this case appears to be somewhat greater than usually obtains. The total chloride content of the sol is 1.56 × 10^{-3} mols per liter. More than ten percent of this remains in the coagulum even in the presence of twice the precipitation concentration of K_2SO_4. From the form of the chloride displacement curve it is apparent that relatively large con-

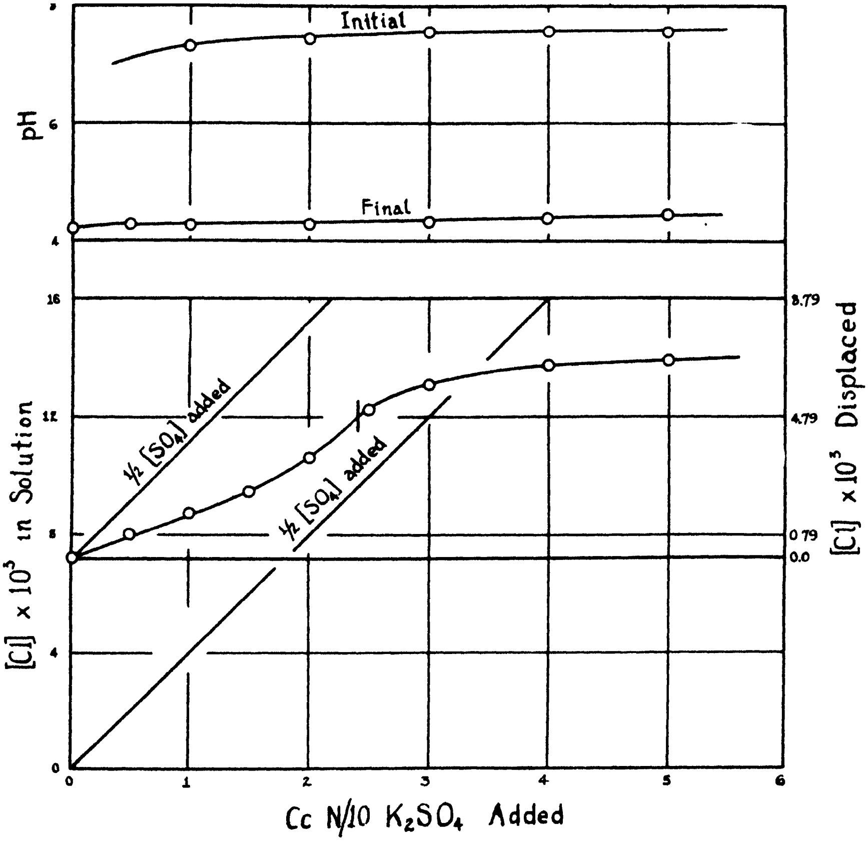

Fig. 3

Titration Curves for Al_2O_3 Sol II with N/10 K_2SO_4

centrations of electrolyte would not displace all the chloride from the oxide. The added sulfate is almost completely adsorbed from solutions up to and including the precipitation value.

In accord with the observations on Sol I, the change in pH value during coagulation is quite small, being but 0.06 pH greater at the precipitation value than the value for the sol. Since the form of the chloride displacement curve shows that agglomeration is taking place during the stepwise addition of the electrolyte, one might expect the pH value to decrease slightly. But this is opposed by the adsorption of hydrogen ion to minimize the action of the adsorbed sulfate ion. The net effect is the slight rise in pH value observed. The pH value of the salt is slightly above 7 but this slight alkaline reaction would influence the pH value of the sol but little if at all, since K_2SO_4 possesses little or no alkali reserve.

Titration with $K_2C_2O_4$. The observations with $K_2C_2O_4$ as precipitating electrolyte are given in Table IV and plotted in Fig. 4. In order to show more clearly the form of the chloride displacement curve the chloride concentration is henceforth plotted on a larger scale. The size of the figure is kept approximately the same by eliminating the lower portion between 0 and 6×10^{-3} [Cl] which lies within the chloride ion concentration of the original sol. The curve for "1/2[C_2O_4]added" obviously begins at 0, 0.

TABLE IV

Titration of Al_2O_3 Sol II with $K_2C_2O_4$

Cc N/10 $K_2C_2O_4$ to 20 cc sol. Total volume 25 cc	π volts	α Cl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	½ [C_2O_4] added $\times 10^3$	pH final	pH initial
0.0	0.0635	6.78	7.21	0.0	0	4.20	—
0.5	0.0625	7.00	7.47	0.26	2	4.44	—
1.0	0.0610	7.37	7.87	0.66	4	4.61	7.80
1.5	0.0594	7.84	8.40	1.19	6	4.73	—
2.0	0.0580	8.28	8.90	1.69	8	4.85	7.83
2.5	0.0555	9.14	9.85	2.64	10	5.00	—
3.0	0.0511	10.84	11.78	4.57	12	5.68	7.85
4.0	0.0498	11.41	12.43	5.22	16	7.08	8.03
5.0	0.0496	11.45	12.47	5.26	20	7.16	8.15

It will be noted that the chloride displacement curve falls slightly below that for sulfate and the precipitation value is somewhat higher than for sulfate as was true for Sol I and for the reason already given. However, the curve with oxalate rises more rapidly as the precipitation value is approached so that the amount of chloride displaced at the precipitation value is approximately the same with both electrolytes.

The pH values of the sol-electrolyte mixtures are somewhat greater than that of the sol, increasing gradually to the precipitation value and then rising sharply. This behavior is exactly what would be expected under the circumstances. The electrolyte is slightly alkaline owing to hydrolysis as follows: $K_2C_2O_4 + H_2O \leftrightarrows KOH + KHC_2O_4$. It thus possesses an alkali reserve which neutralizes to a certain extent the acidity of the sol, the effect being more marked as the precipitation value is approached. Above the precipitation concentration, the pH value rises sharply approaching that of the pure electrolyte. This is what it should do since the neutralized coagulum settles out leaving the supernatant liquid which contains only chloride and the excess oxalate.

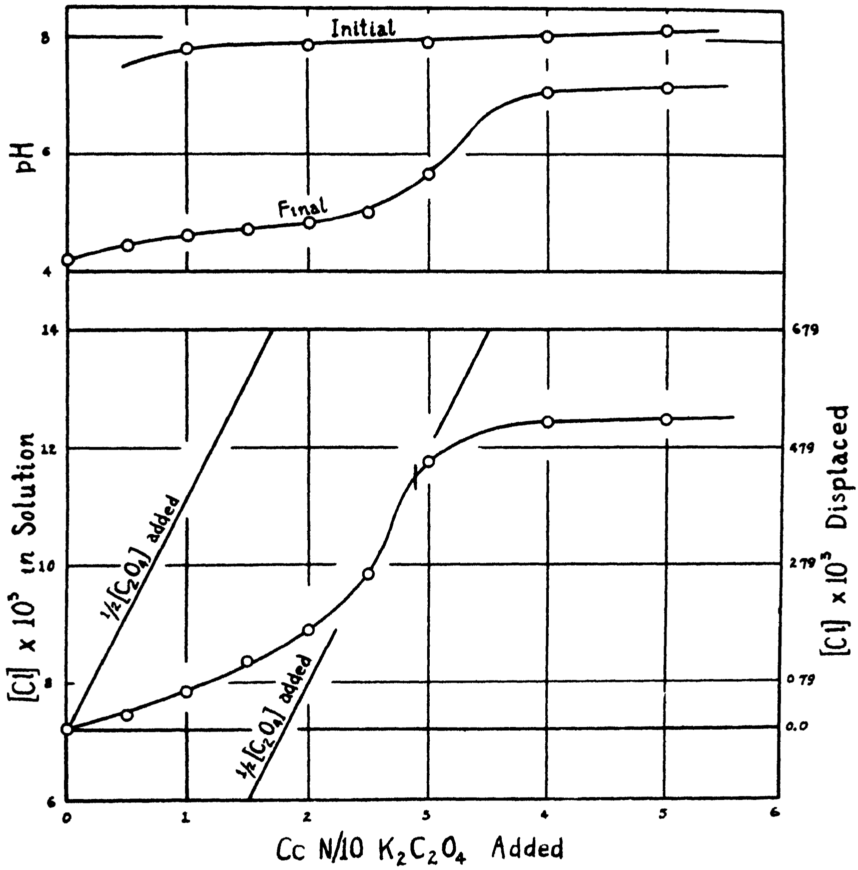

FIG. 4
Titration Curves for Al_2O_3 Sol II with $N/10$ $K_2C_2O_4$

Titration with $K_3C_6H_5O_7$. An $N/10$ $K_3C_6H_5O_7$ solution was prepared by taking 1/30 of the molecular weight of the salt per liter. Since such a solution contains relatively few trivalent ions as compared with the number of divalent and univalent ions, it is not permissible to compare the data given in Table V and shown graphically in Fig. 5 with the corresponding data obtained

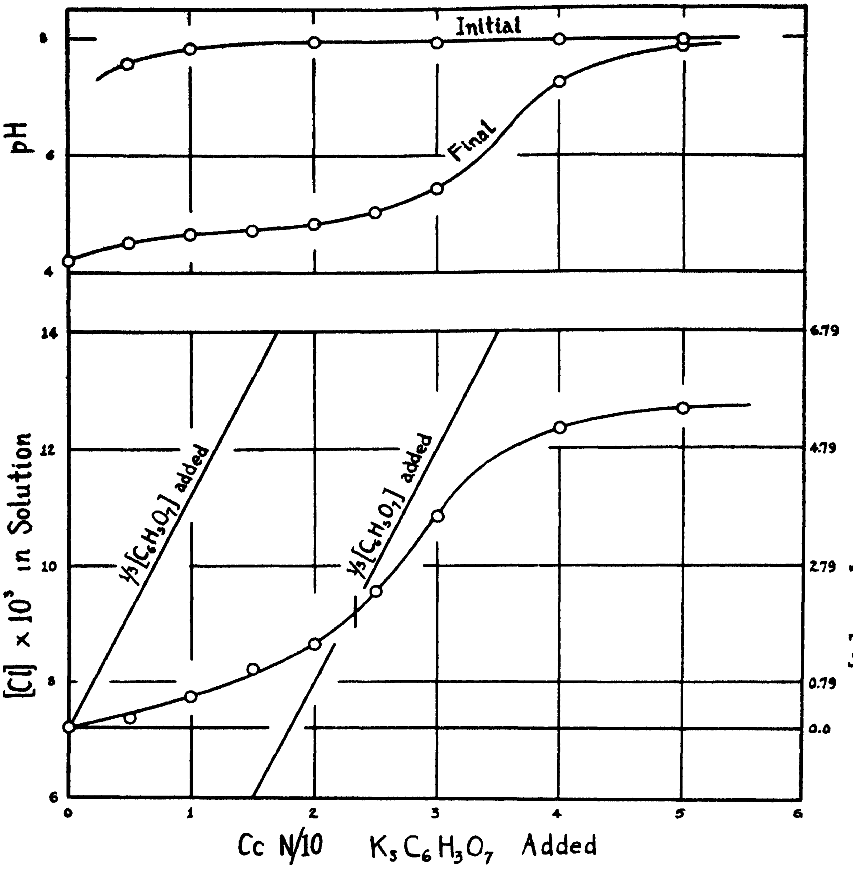

Fig. 5

Titration Curves for Al_2O_3 Sol II with *N*/10 $K_3C_6H_3O_7$

Table V

Titration of Al_2O_3 Sol II with $K_3C_6H_3O_7$

Cc *N*/10 $K_3C_6H_3O_7$ to 20 cc sol. Total volume 25 cc	π volts	α Cl^- × 10^3	[Cl] × 10^3	[Cl] displaced × 10^4	⅓ [$C_6H_3O_7$] added × 10^3	pH final	pH initial
0.0	0.0635	6.78	7.21	0.0	0	4.20	—
0.5	0.0628	6 87	7.32	0.11	2	4.51	7.57
1.0	0.0615	7.23	7.72	0.51	4	4.65	7.83
1.5	0.0600	7.67	8.21	1.00	6	4.71	—
2.0	0.0588	8.03	8.61	1.40	8	4.85	7.90
2.5	0.0563	8.85	9.53	2.31	10	5.03	—
3.0	0.0532	10.00	10.82	3.61	12	5.42	7.93
4.0	0.0500	11.32	12.33	5.12	16	7.24	7.98
5.0	0.0494	11.60	12.65	5.44	20	7.89	7.98

with sulfate and oxalate, since the concentration of effective ions in the citrate solution is probably lower than with the other salts.

It will be noted that the precipitation concentration of the $M/30$ citrate is somewhat lower than with either $N/10$ sulfate or oxalate and that the chloride displaced at the precipitation value is less than with either of the above mentioned salts. This is accounted for by the fact that the neutralization of the charge on the particles is due in part to the strongly adsorbed trivalent ion which has a more marked discharging action than either monovalent or divalent anions. Accordingly, to the extent that the trivalent ion contributes to the lowering of the charge on the particles to the point of coagulation, less needs to be adsorbed and correspondingly less chloride will be displaced at the precipitation value. This behavior is similar although much less pronounced than was observed with the trivalent ferricyanide on ferric oxide sol.[1]

The increase in pH value during the titration process is comparable to that of potassium oxalate but is somewhat more pronounced owing to the more marked buffering action of alkali citrate solutions.

Titration with $NH_4C_2H_3O_2$. Since the precipitating power of the univalent acetate ion is relatively weak, it was necessary to use a 2 normal solution of the salt to effect coagulation within 5 cc of electrolyte in 20 cc of sol. The titration data are given in Table VI and plotted in Fig. 6. The chloride displacement curve does not have the S-shape and there is no point of inflexion at the point where coagulation is complete. The reason is obvious to one carrying out the experiments. The addition of as little as 0.5 cc of the 2 N salt in a total volume of 25 cc caused a perceptible increase in the cloudiness of the sol. This cloudiness increased gradually with larger additions of electrolyte until finally the particles grew to a sufficient size to settle out. The form of the chloride displacement curve is a manifestation of this gradual

TABLE VI

Titration of Al_2O_3 Sol II with $NH_4C_2H_3O_2$

Cc $N/10$ $NH_4C_2H_3O_2$ to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	$[C_2H_3O_2]$ added $\times 10^3$	pH final	pH initial
0.0	0.0635	6.78	7.21	0.0	0	4.20	—
0.5	0.0578	8.35	8.97	1.76	40	5.55	6.51
1.0	0.0553	9.20	9.92	2.71	80	5.86	6.57
1.5	0.0526	10.11	10.94	3.73	120	6.06	—
2.0	0.0512	10.80	11.71	4.50	160	6.16	6.63
3.0	0.0491	11.72	12.78	5.57	240	6.30	6.66
4.0	0.0474	12.52	13.71	6.50	320	6.30	6.71
5.0	0.0465	12.97	14.22	7.01	400	6.46	6.74

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[1] J. Phys. Chem., **34**, 1 (1931).

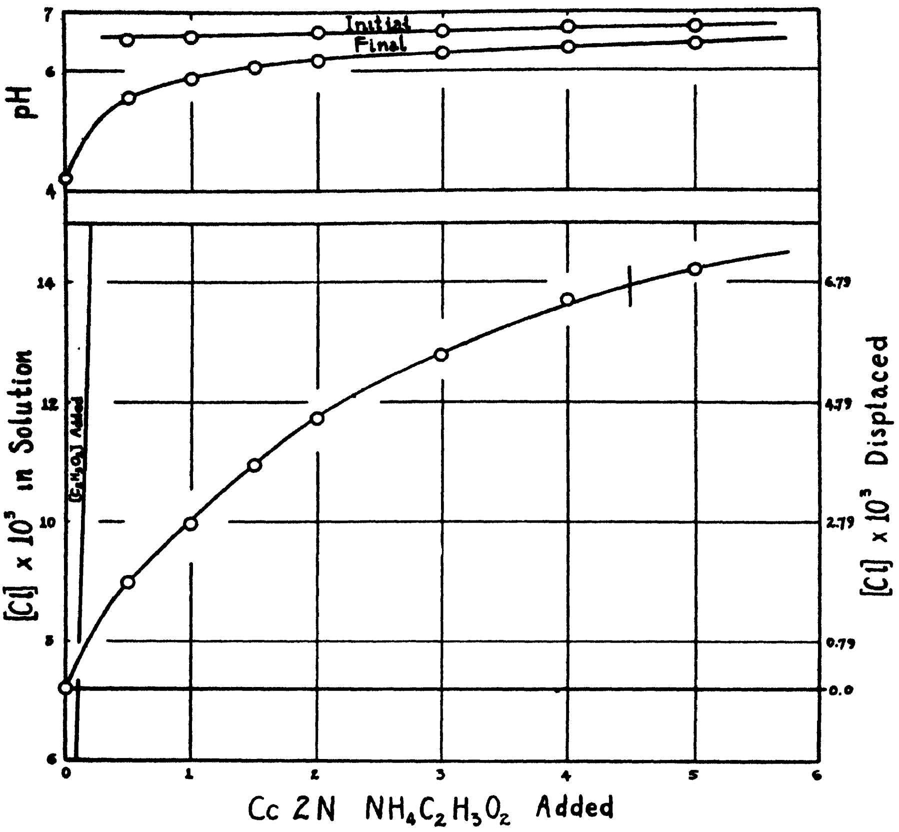

FIG. 6
Titration Curves for Al_2O_3 Sol II with 2 *N* $NH_4C_2H_3O_2$

TABLE VII

Titration of Al_2O_3 Sol II with KNO_3

Cc *N* KNO_3 to 20 cc sol. Total volume 25 cc	π volts	$\alpha Cl^- \times 10^3$	$[Cl] \times 10^3$	[Cl] displaced $\times 10^3$	$[KNO_3]$ added $\times 10^3$	pH final	pH initial
0.0	0.0635	6.78	7.21	0.0	0	4.21	——
0.5	0.0608	7.36	7.86	0.65	40	4.32	——
1.0	0.0605	7.52	8.05	0.84	80	4.38	6.19
2.0	0.0605	7.52	8.05	0.84	160	4.44	6.22
3.0	0.0606	7.50	8.03	0.82	240	4.48	6.24
4.0	0.0606	7.50	8.03	0.82	320	4.51	6.27
5.0	0.0605	7.52	8.05	0.84	400	4.52	6.28
5 in 10	0.0668	5.88	6.24		1000	——	——
10 in 10	0.0729	4.64	4.90		2000	——	——

lowering of charge and the consequent gradual increase in particle size without a distinct zone of rapid coagulation such as obtains with multivalent precipitating ions.

The increase in pH value on adding acetate to the acid sol, the value at higher concentrations approaching that of the pure electrolyte, is in entire accord with the well known buffer action of acetates.

Titration with KNO_3. A 2 *N* solution of KNO_3 was employed in these experiments although the precipitation concentration is higher than 5 cc of 2 *N* solution in 25 cc of sol. From the data in Table VII which is plotted in Fig. 7 it would appear that the observed chloride displacement rises to a maximum value in the presence of but 1 cc of 2 *N* solutions. This value remains constant until more than 5 cc of 2 *N* solution is added and thereafter it drops off. This observed behavior is undoubtedly due in part at least to the limitations of the experimental method. Certainly the apparent falling off in the chloride displaced at higher concentrations cannot be right and is probably the result of an oxidation-reduction reaction involving calomel and KNO_3 which becomes quite pronounced with the more concentrated KNO_3 solutions. The observations show clearly the lower precipitating power and chloride displacing power of univalent nitrate as compared even with univalent acetate which in turn shows a much lower displacing and precipitating action than the multivalent anions.

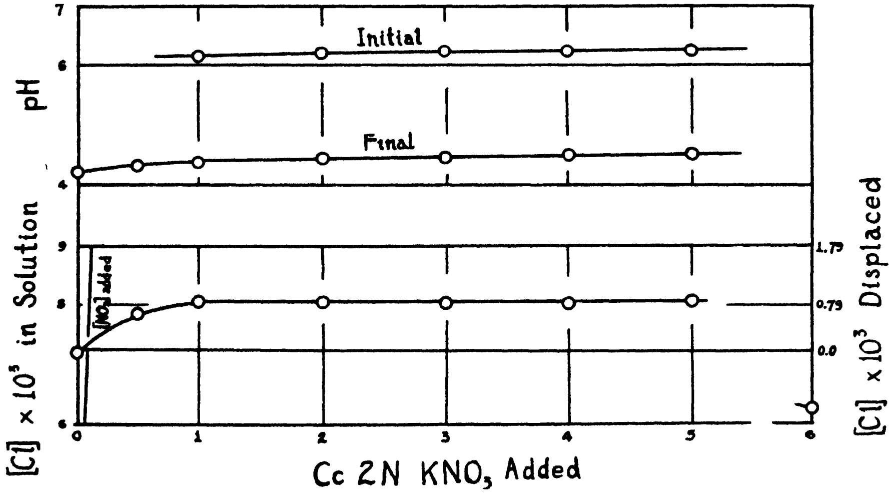

Fig. 7
Titration Curves for Al_2O_3 Sol II with 2 *N* KNO_3

As would be expected, the change in pH value on adding KNO_3 solution to the acid sol is negligible as compared with acetate, citrate, or oxalate and is of the same order of magnitude as that for the same concentration of K_2SO_4. A test showed that the addition to the sol of 0.1 cc of 2 *N* KNO_3 in a total volume of 25 cc, which would be almost enough to effect coagulation if it were K_2SO_4, causes a rise in pH value from 4.20 to 4.25.

Observations on Alumina Sol III

It will be recalled that Sol III was prepared by hydrolysis of $AlCl_3$ solution while Sols I and II were formed by peptization of "grown" Al_2O_3 formed by the direct action of water on amalgamated aluminum. If the hydrolysis of $AlCl_3$ under conditions that lead to sol formation gives poly-ol basic aluminum salts of the Werner type as assumed by Thomas and Whitehead and if the change in pH value on adding salts to such sols is due to displacement of OH groups from the complex which unite with H to form H_2O, then one might expect to find some difference in the behavior of the two types of sols toward electrolytes. As the following experiments show there is some difference in behavior but it is in the direction opposite to that which would be predicted on the basis of the Thomas-Whitehead hypothesis.

Titration with K_2SO_4. The results of adding $N/10$ K_2SO_4 to Sol III in gradually increasing amounts are given in Table VIII and plotted in Fig. 8.

TABLE VIII

Titration of Al_2O_3 Sol III with K_2SO_4

Cc $N/10$ K_2SO_4 to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	½ [SO_4] added $\times 10^3$	pH final	pH initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	——
0.5	0.0622	7.02	7.50	0.50	2	——	——
1.0	0.0600	7.67	8.21	1.21	4	5.11	7.33
1.5	0.0582	8.22	8.82	1.82	6	5.06	——
2.0	0.0560	8.96	9.66	2.66	8	5.02	7.43
2.5	0.0539	10.07	10.90	3.90	10	4.01	——
3.0	0.0523	10.31	11.18	4.18	12	4.91	7.56
4.0	0.0516	10.63	11.54	4.54	16	4.86	7.56
5.0	0.0513	10.76	11.70	4.70	20	4.86	——

The form of the chloride displacement curve is essentially the same as that obtained with Sol II. The particles of the sol formed from "grown" alumina are less hydrous and the precipitate less gelatinous than that obtained from Sol III and the precipitation value is slightly higher. Approximately 20 percent of the total chloride content is retained by the precipitate so that it cannot be detected potentiometrically after adding 5 cc of the electrolyte to 20 cc of sol. This is somewhat more than was observed under similar conditions with the less hydrous Sol II.

The change in pH value is significant. It will be noted that there is a slight decrease in pH value during the stepwise addition of electrolyte. In this case it appears that the loss of adsorbed hydrogen ions by the particles during the coalescence which accompanies the lowering of the charge is slightly greater than the opposing tendency to adsorb hydrogen ion from solution to maintain the charge. Obviously, the change is in the wrong direction to account for it by assuming the displacement of OH groups from a Werner complex by the sulfate radicals.

Whatever difference of opinion there may be as regards the explanation of the phenomenon, there appears to be little or no question about the accuracy of the findings. Observations of the change in pH value on adding varying amounts of sulfate solution were repeated three times using both the hydrogen and the "quinhydrone" electrodes. Closely agreeing results were obtained in the measurements and there was always a definite, unmistakable decrease in pH value on adding the electrolyte to the sol. There is of course nothing unusual in this behavior from the standpoint of the adsorption theory. For, as already pointed out, the shifting of the adsorption equilibria on addition to the sol of a neutral salt of a strong acid and a strong base would be expected to increase slightly, decrease slightly, or leave unchanged the pH value depending on the relative magnitude of two opposing tendencies.

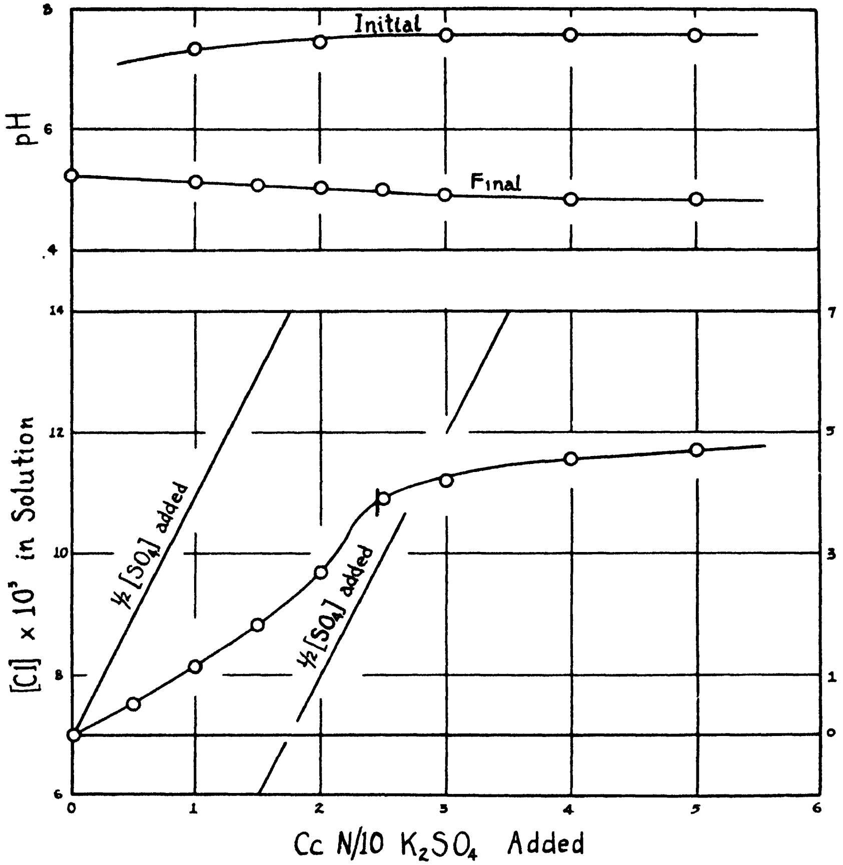

FIG. 8
Titration Curves for Al_2O_3 Sol III with $N/10$ K_2SO_4

From the observed small decrease in pH value on the coagulation of Sol III with potassium sulfate and of a small increase in the pH value on coagulating Sol II with the same salt, one would expect the increase in pH value with a buffering salt like potassium citrate to be proportionately less with Sol III than with Sol II for a given addition of electrolyte. That such is the case will be shown in the subsequent observations.

Titration with $K_3C_6H_5O_7$. The displacement of chloride and the change in pH value on titrating Sol III with citrate are given in Table IX and Fig. 9.

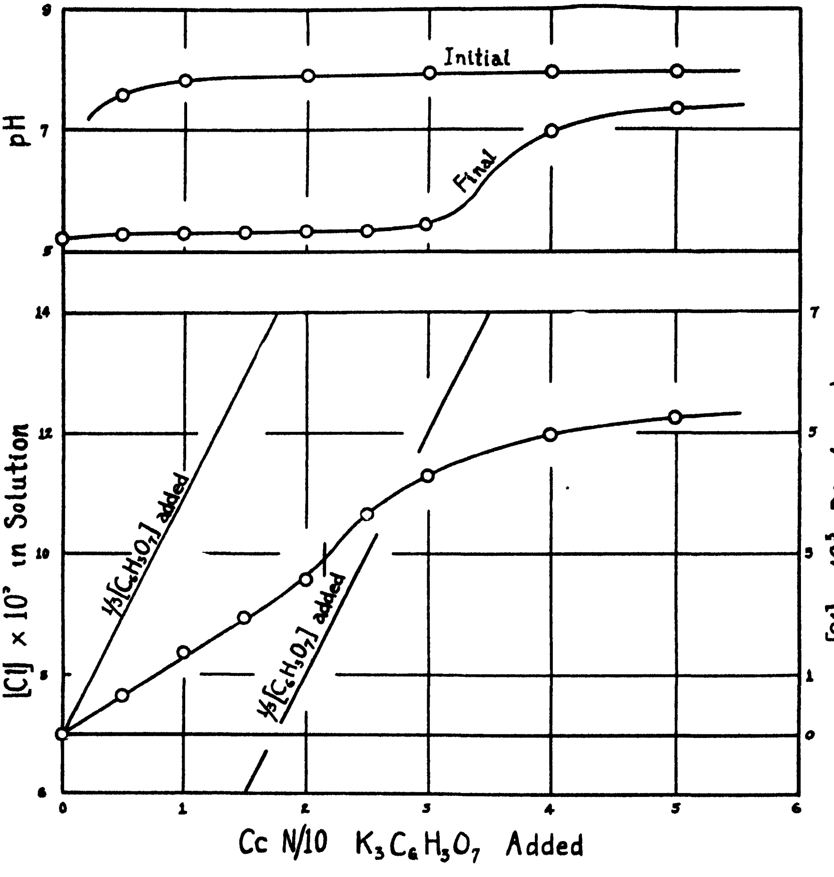

FIG. 9
Titration Curves for Al_2O_3 Sol III with N/10 $K_3C_6H_5O_7$

As in the case of sulfate the chloride displacement curve is somewhat lower than that with the "grown" alumina sol.

As predicted, the increase in pH value is less on adding citrate to Sol III than to Sol II. Indeed the increase is but 0.20 pH until the colloid precipitates out whereupon the pH value of the supernatant solution, due in large measure to unadsorbed citrate, approaches that of the pure citrate solution.

Titration with $K_2C_2O_4$. The observations with $K_2C_2O_4$ as precipitating electrolyte are given in Table Xa and Fig. 10, the points being represented

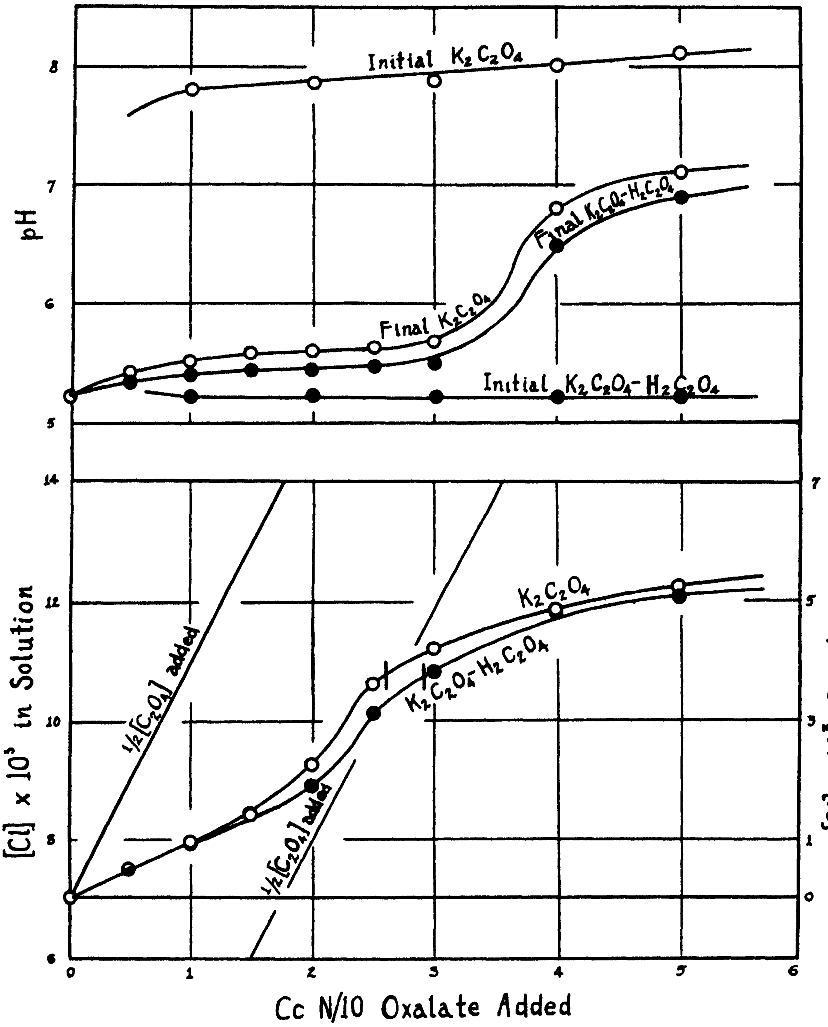

FIG. 10
Titration Curves for Al_2O_3 Sol III with N/10 $K_2C_2O_4$ and N/10 $K_2C_2O_4$-$H_2C_2O_4$ Mixtures

TABLE IX

Titration of Al_2O_3 Sol III with $K_3C_6H_3O_7$

Cc N/10 $K_3C_6H_3O_7$ to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	|Cl| $\times 10^3$	[Cl] displaced $\times 10^3$	$\frac{1}{3}[C_6H_3O_7]$ added $\times 10^3$	pH final	pH initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	——
0.5	0.0617	7.17	7.66	0.66	2	5.25	7.57
1.0	0.0595	7.81	8.38	1.38	4	5.28	7.83
1.5	0.0580	8.28	8.90	1.90	6	5.30	——
2.0	0.0564	8.82	9.50	2.50	8	5.32	7.90
2.5	0.0536	9.86	10.64	3.64	10	5.37	——
3.0	0.0522	10.39	11.27	4.27	12	5.43	7.93
4.0	0.0508	10.97	11.93	4.93	16	6.97	7.98
5.0	0.0501	11.27	12.26	5.26	20	7.34	7.98

TABLE Xa

Titration of Al_2O_3 Sol III with $K_2C_2O_4$

Cc N/10 $K_2C_2O_4$ to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	|Cl| $\times 10^3$	[Cl] displaced $\times 10^3$	$\frac{1}{2}[C_2O_4]$ added $\times 10^3$	pH final	pH initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	——
0.5	0.0622	7.02	7.50	0.50	2	5.42	——
1.0	0.0608	7.45	7.97	0.97	4	5.50	7.80
1.5	0.0594	7.84	8.40	1.40	6	5.56	——
2.0	0.0570	8.62	9.26	2.26	8	5.61	7.83
2.5	0.0537	9.80	10.60	3.60	10	5.62	——
3.0	0.0523	10.31	11.18	4.18	12	5.66	7.88
4.0	0.0510	10.88	11.82	4.82	16	6.81	8.03
5.0	0.0500	11.32	12.32	5.32	20	7.12	8.15

by dots. These data merely confirm previous observations with this salt. Here also the increase in pH value for a given amount of added electrolyte is less than was observed with Sol II.

Since potassium oxalate is alkaline, the question is naturally raised as to what will be the effect of rendering it slightly acid before the titration by the addition of oxalic acid keeping the total oxalate concentration the same.[1] The results of some observations with an N/10 oxalate solution brought to about the same pH value as the sol by adding a small amount of N/10 oxalic acid to N/10 $K_2C_2O_4$, are given in Table Xb and shown graphically in Fig. 10, the points on the curves being represented by circles.

The behavior with the potassium oxalate-oxalic acid mixture is in line with what would be expected from earlier observations of Weiser and Porter.[2] The addition of the mixture supplies a small hydrogen ion reserve which is

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[1] Cf. Thomas and Whitehead: J. Phys. Chem., **35**, 27 (1931).

[2] J. Phys. Chem., **31**, 1383 (1927).

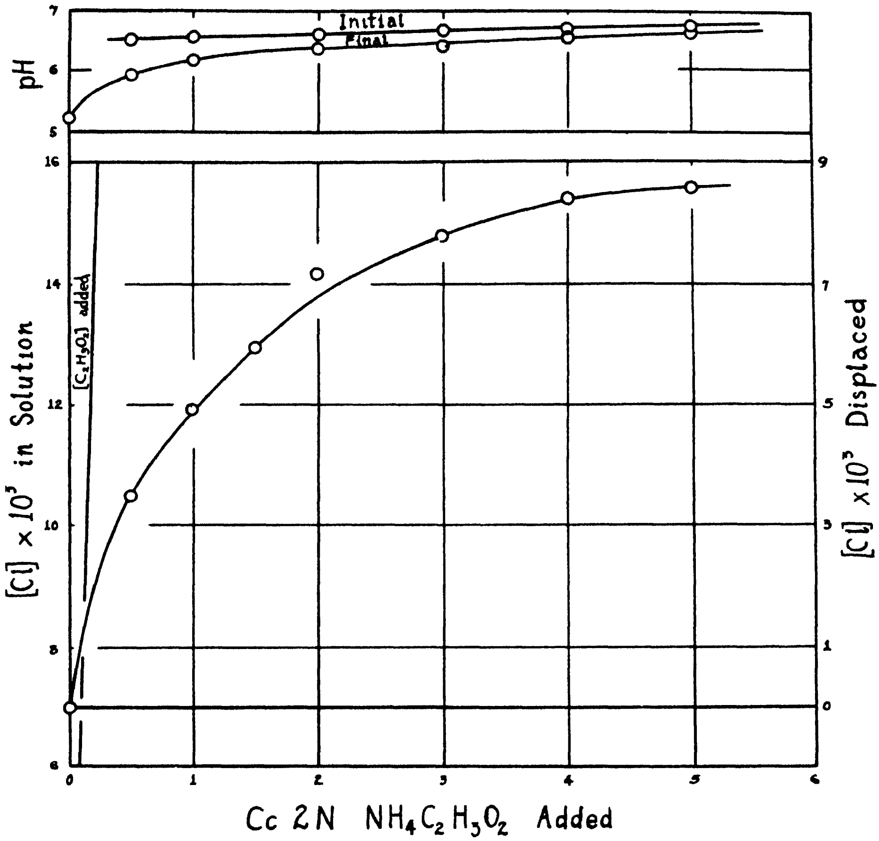

Fig. 11
Titration Curves for Al_2O_3 Sol III with 2 N $NH_4C_2H_3O_2$

Table Xb

Titration of Al_2SO_3 Sol III with $K_2C_2O_4$-$H_2C_2O_4$ Mixture

Cc N/10 oxalate to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^4$	[Cl] displaced $\times 10^3$	½$[C_2O_4]$ added $\times 10^3$	pH final	pH initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	——
0.5	0.0620	7.09	7.56	0 56	2	5.34	——
1.0	0.0610	7.37	7.88	0.88	4	5.39	5.20
1.5	0.0592	7.94	8.51	1.51	6	5.43	——
2.0	0.0580	8.28	8.90	1.90	8	5.47	5.21
2.5	0.0549	9.35	10.09	3.09	10	5.46	——
3.0	0.0535	9.88	10.80	3.80	12	5.48	5.22
4.0	0.0511	10.85	11.80	4.80	16	6.51	5.22
5.0	0.0505	11.10	12.17	5.17	20	6.91	5.22

promptly adsorbed by the colloidal particles, a phenomenon which results in an increase in the charge on the particles and hence on the stability of the sol. Thus, the sol acts as a buffer owing to its adsorption capacity. This behavior is not unusual, as Bovie[1] has demonstrated in an interesting way the buffer action of charcoal which acts by virtue of its adsorbing capacity.

It is, of course, a mistake to assume that the oxalate concentration remains constant on mixing equivalent solutions of $K_2C_2O_4$ and $H_2C_2O_4$ since the following reaction takes place: $K_2C_2O_4 + H_2C_2O_4 \rightarrow 2KHC_2O_4$. The net result of the increased stability of the sol and the proportionately larger amount of univalent bioxalate ion in the salt-acid mixtures, is a chloride displacement curve that runs under that for $K_2C_2O_4$ and a precipitation concentration for the salt-acid mixture that is distinctly higher than for the salt alone.

The pH value curve on adding the salt-acid mixture to the sol is appreciably lower than that for the slightly alkaline salt as would be expected. But hydrogen ion is so strongly adsorbed by the colloidal particles that above the precipitation value, the pH value promptly mounts toward that of a $K_2C_2O_4$ solution although, here also, the curve runs below that when oxalate alone is used.

Titration with $NH_4C_2H_3O_2$. The data with ammonium acetate as precipitating electrolyte are given in Table XI and represented graphically in Fig. 11.

TABLE XI

Titration of Al_2SO_3 Sol III with $NH_4C_2H_3O_2$

Cc 2 *N* $NH_4C_2H_3O_2$ to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[$C_2H_3O_2$] added $\times 10^3$	pH final	pH initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	——
0.5	0.0540	9.68	10.46	3.46	40	5.93	6.51
1.0	0.0508	10.97	11.92	4.92	80	6.19	6.57
1.5	0.0488	11.86	12.92	5.92	120	6.35	——
2.0	0.0465	12.97	14.22	7.22	160	6.40	6.63
3.0	0.0452	13.64	14.82	7.82	240	6.50	6.66
4.0	0.0445	14.02	15.44	8.44	320	6.57	6.71
5.0	0.0443	14.13	15.55	8.55	400	6.62	6.74

The chloride displacement curve follows the same general course as observed with Sol II. By comparison with Fig. 6 it will be seen that the amount of chloride displaced by the same concentration of acetate is relatively greater with the sol under observation than with Sol II.

The pH values of the sol-acetate mixtures are, of course, higher than for the sol alone, approaching that of the pure electrolyte when high concentrations are added.

Titration with KNO_3. The titration data in Table XII which are plotted in Fig. 12, show that the displacing action of nitrate like that of acetate is

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[1] J. Med. Research, 33, 295 (1915).

TABLE XII

Titration of Al_2O_3 Sol III with KNO_3

Cc $N/10$ KNO_3 to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	[NO_3] added $\times 10^3$	pH final	pH initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	——
0.5	0.0585	8.14	8.73	1.73	40	5.39	——
1.0	0.0584	8.16	8.75	1.75	80	5.46	6.19
2.0	0.0582	8.22	8.82	1.82	160	5.50	6.22
3.0	0.0575	8.45	9.08	2.08	240	5.51	6.27
4.0	0.0590	7.97	8.54	1.54	320	5.51	6.27
5.0	0.0600	7.67	8.21	1.21	400	5.51	6.28

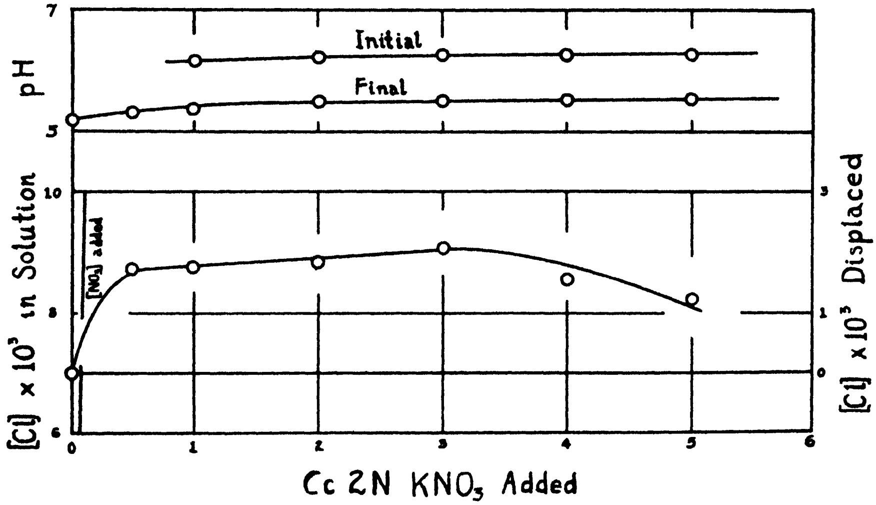

FIG. 12
Titration Curves for Al_2O_3 Sol III with 2 N KNO_3

greater for the sol under observation than that for Sol II. Unfortunately the limitations of the potentiometric measurements do not give the true course of the chloride displacement at the higher concentrations of KNO_3. As would be expected the pH value changes but little during the coagulation process.

Summary. A summary of the observations on chloride displacement and pH value for the same normal concentration of KNO_3, $NH_4C_2H_3O_2$, K_2SO_4, and $K_2C_2O_4$ is given in Fig. 13. As already pointed out, the data with $K_3C_7H_3O_6$ are not strictly comparable with those of sulfate and oxalate and so are not included in the figure. If the citrate solution contained largely trivalent ions the first part of the chloride displacement curve with this salt would be appreciably higher than that for the same normal concentration of divalent ions. The order of chloride displacing power below the precipitation concentration for the sol is: citrate > sulfate > oxalate > acetate > nitrate. Above the precipitation value where the supernatant oxalate solution becomes less acid, oxalate and sulfate exchange places. This is due to the fact that the oxalate solution contains relatively more of univalent bioxalate ion in the more acid range and relatively more of the strongly adsorbed bivalent oxalate ion in the less acid range beyond the precipitation value. The displacement curve with oxalate never rose above that for sulfate when the more acid Sols I and II were used.

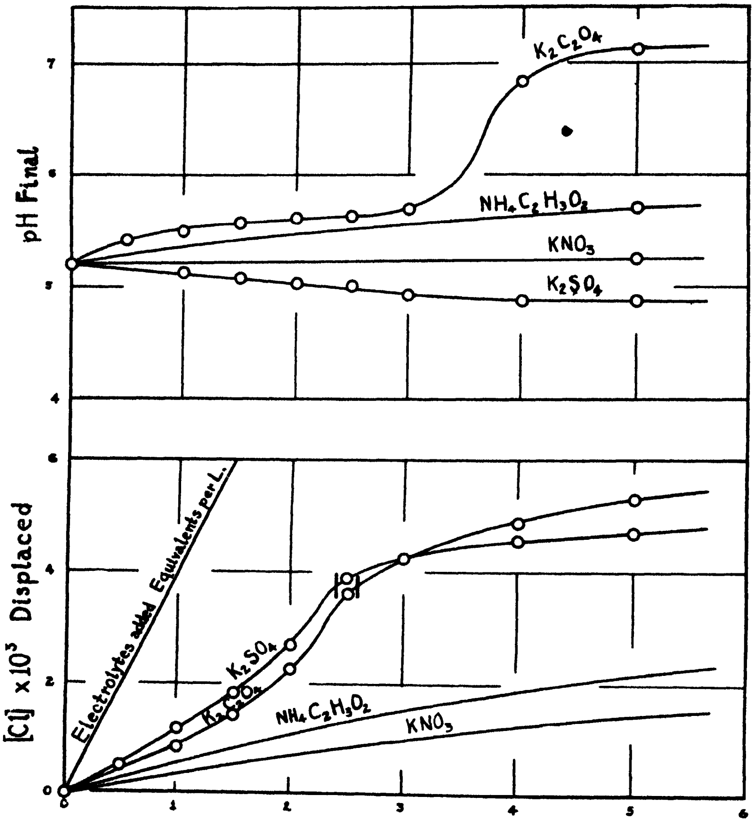

FIG. 13
Comparison of Titration Curves for Al_2O_3 Sol III with Different Electrolytes

The order of precipitating power of the several salts is: citrate > sulfate > oxalate > acetate > nitrate. This order is identical with the order of chloride displacing power.

A comparison of the pH value and chloride displacement curves on adding the several electrolytes to alumina sols reveals a distinct difference in the order. Thus the order in which the alkali salts increase the pH value of the several sols is: citrate > oxalate > acetate > nitrate > sulfate. It will be recalled that the addition of sulfate actually raises slightly the pH value of Sol III and that nitrate has but little effect. As would be expected, the most marked tendency to raise the pH value of the acid sols is manifested by the electrolytes with a buffering action, by virtue of their alkali reserve. It should be pointed out that it is not strictly accurate to compare the pH value curves in the region just above and below the precipitation concentration of salts having multivalent anions with the curves for the same equivalent concentration of the salts of univalent ions, since such concentrations of the latter salts affect the stability of the sol much less than the former and so influence the adsorption equilibria to a much smaller extent. The order at the precipitation concentration is: acetate > citrate, oxalate > nitrate > sulfate.

Effect of Ageing on the pH Value of Sols

In the introductory paragraphs it was pointed out that ageing a hydrous oxide sol leads to some coalescence and agglomeration of particles and a decrease in their hydrous character with a consequent decrease in specific surface. This should result in a falling off in the pH value of a sol stabilized by preferential adsorption of hydrogen ion, owing to the release of some of the adsorbed ions accompanying the decrease in surface. This change should be less in a sol that had been heated in the course of preparation than in one prepared at room temperature. Some observations made in the course of this investigation which have been brought together in Table XVIII support the above conclusions. With none of the sols was there any indication of an increase in pH value on standing such as Thomas and Whitehead observed with sols peptized by HCl. As already suggested it seems probable that the initial increase which they observed resulted from removal of H ions by direct action of the acid with the oxide.

TABLE XVIII

Sol I Peptization of grown Al_2O_3 with $AlCl_3$		Sol II Peptization of grown Al_2O_3 with $AlCl_3$		Sol III Hydrolysis of $AlCl_3$ followed by hot dialysis	
Time	pH value	Time	pH value	Time	pH value
2 days	4.42	1 day	4.35	1 day	5.23
3 weeks	4.31	3 weeks	4.20	2 weeks	5.20
3 months	4.03	2.5 months	4.01	2 months	5.12

Structure of the Alumina Micelles

The experimental results given above confirm and extend the observations made on ferric oxide sols. To account for the behavior of alumina sols, during the process of coagulation by electrolytes, the structure of the colloidal particle may be represented diagrammatically as in Fig. 14. Exclusive of the

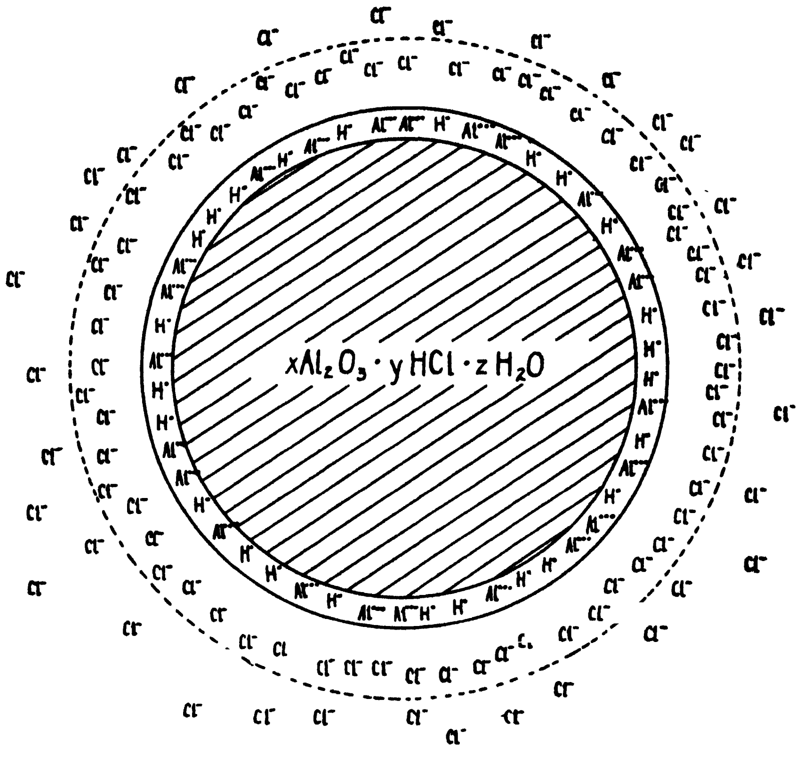

Fig. 14

Diagrammatic representation of the constitution of an alumina micelle stabilized by preferential adsorption of $H^{\cdot}$ and $Al^{\cdots}$ ions. The Cl' ions beyond the dotted circle can be estimated potentiometrically.

outer layer the composition can be indicated by some point in the three component diagram $Al_2O_3 \cdot HCl \cdot H_2O$. Since the relative amounts of the several components vary with the conditions of formation, the composition is formulated: $xAl_2O_3 \cdot yHCl \cdot zH_2O$. The outer capsule is an ionic double layer. The inner portion of this layer consists of adsorbed hydrogen and aluminum ions in adsorption equilibrium with the cations in the intermicellar liquid. The outer portion consists of a diffuse layer of chloride ions most of which are held by the electrostatic attraction of the adsorbed positive inner layer; but a part of which, because of a relatively higher kinetic energy, exert sufficient osmotic repulsive force against the attraction of the double layer to influence the calomel electrode and so may be detected potentiometrically. The latter ions are represented in the diagram beyond the dotted line.

This diagrammatic representation of the structure of the micelle indicates the source of its positive charge, its variability in composition, and the fact that not all of the chloride is readily displaced by the addition of other ions. If a salt with a multivalent anion such as potassium sulfate is added to the sol, there is a change in the double layer which is represented diagrammatically in Fig. 15. The strongly adsorbed sulfate ion goes into the double layer closer

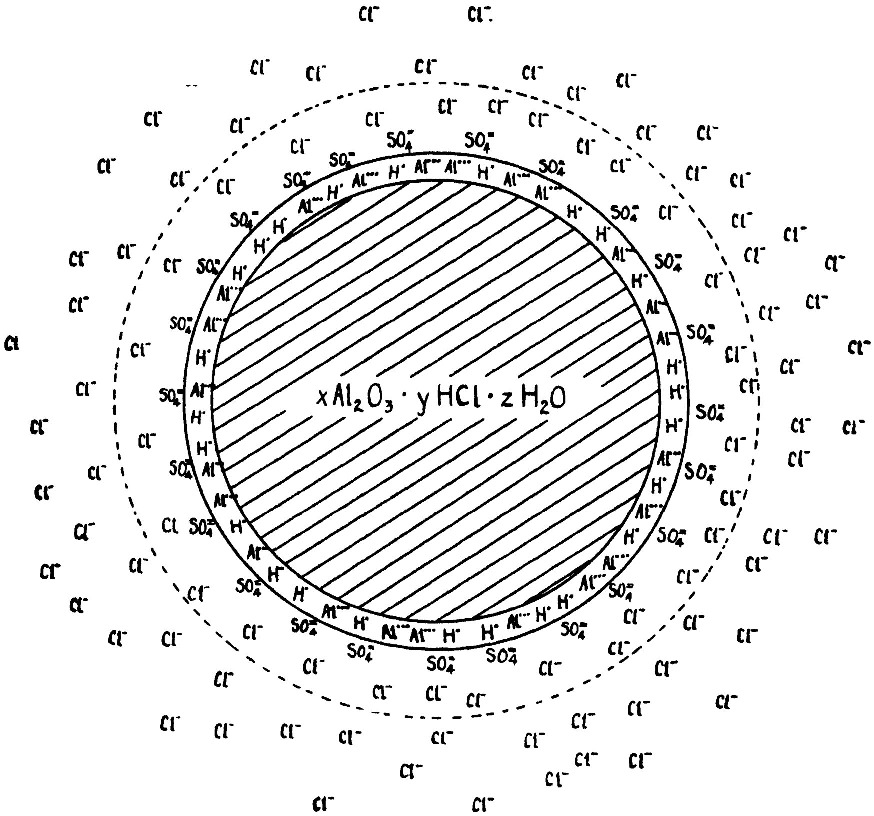

Fig. 15

Diagrammatic representation of the constitution of the alumina micelle shown in Fig. 14 after the addition of sulfate.

to the inner layer and displaces chloride as indicated. The differences between the chloride measured potentiometrically in the original sol and that after the addition of sulfate represents the amount of chloride displaced by sulfate. A glance at the several curves discloses that in all cases the amount of chloride displaced is less than the amount of electrolyte added. Thus in the case of sulfate the displaced chloride is less than one-half the equivalent of sulfate added. Since up to and including the precipitation value most of the sulfate is adsorbed, it may be wondered why an equivalent amount is not displaced. The reason is that a part of the sulfate which enters the layer corresponds to chloride measured potentiometrically in the original sol. At the precipitation value of the strongly adsorbed multivalent ions, the amount of chloride in the supernatant solution approximates that of the multivalent ion adsorbed. But the observed concentration of chloride is the sum of that originally present and that displaced in the adsorption process.

The lowering of the charge on the particles following the addition of small amounts of multivalent ions is due to the much stronger adsorption of multivalent ions than that of univalent chloride. The result is that the adsorbed ions are drawn closer to the inner layer, as indicated in the diagram, thus reducing the thickness of the double layer. Since the potential difference between two layers of opposite sign with constant charge density is directly proportional to the distance between them, it necessarily follows that the thinner layer will have a lower charge. In case the adsorbability of ions is determined by valency alone, multivalent ions will have a stronger discharging action than univalent ions because the larger charge on the former will cause them to be attracted more closely to the inner layer with the consequent lowering of charge. As is well known, a similar discharging action with univalent precipitating ions takes place only at relatively high concentrations.

The lowering of the charge on the particles results in coalescence and agglomeration of the particles with a consequent decrease in specific surface. This manifests itself in an increase in the amount of chloride displaced for a given increment in the multivalent ion added as the region of rapid coagulation is approached. Hence the upward bend in the chloride displacement curve with multivalent ions, which becomes more marked in the region of rapid coagulation. Above the coagulation point, the chloride is displaced from the precipitate by exchange adsorption without any marked decrease in specific surface and the curve follows the usual course of the adsorption isotherm. This combination of conditions accounts for the S-shape of the chloride displacement curve with all electrolytes having a high precipitating power and causing rapid coagulation above a critical concentration.

Electrolytes with relatively low precipitating power which do not cause rapid coagulation, in a critical zone, give chloride displacement curves which follow throughout the course of the adsorption isotherms as a result of exchange adsorption and gradual coagulation.

The adsorption of the added anions by the colloidal particles will tend to increase the adsorption of cations and the agglomeration with decrease in specific surface which accompanies the lowering of the charge will tend to decrease the adsorption of both cations and anions. In the sols under observation, the adsorbed hydrogen ion is in equilibrium with a hydrogen ion concentration between 10^{-4} and 10^{-5} mols per liter. The shifting of the adsorption equilibria which accompanies the addition to the sol of a salt of a strong acid and a strong base will increase slightly, decrease slightly, or leave unchanged the pH value depending, in any given case, on the relative magnitude of the two opposing tendencies, above mentioned. With salts such as potassium citrate and ammonium acetate buffer action always renders the pH value of the sol-electrolyte mixtures higher than that of the sol alone.

There appears to be little justification for the assumption that an alumina sol formed by hydrolysis of $AlCl_3$ and dialysis is an indefinite complex poly-ol basic aluminum salt of the Werner type and that the increase in pH value on adding such salts as KNO_3 and K_2SO_4 to the sol is due to displacement of OH groups which unite with $H^{\cdot}$ to form water. Indeed the addition of K_2SO_4 to one such sol caused the pH value to decrease slightly. Finally, there appears to be no more justification for assuming that alumina sols formed by peptization of "grown" alumina with $AlCl_3$ are indefinite complex poly-ol basic aluminum chlorides than for assuming that AgCl sol formed by preferential adsorption of Ag ions is a complex silver subchloride of indefinite composition.

Summary

A study has been made of the change in chloride ion concentration and in pH value during coagulation by the stepwise addition of electrolytes to aluminum sols prepared (a) by peptization of "grown" alumina with $AlCl_3$ and (b) by hydrolysis of $AlCl_3$ and dialysis. The results confirm and extend those obtained by similar observations on ferric oxide sol. The following summary is therefore limited to results which did not appear in the study of the mechanism of coagulation of ferric oxide sol and so constitutes an addendum to the summary given in the first paper.

1. Titration curves are given which show the displacement of chloride from the micelles on adding potassium sulfate, oxalate, citrate, nitrate, and ammonium acetate, stepwise to the different alumina sols.

2. The form of the chloride displacement curve is S-shaped with electrolytes containing multivalent precipitating ions which cause rapid coagulation above a critical concentration. The amount of chloride displaced for a given increment in multivalent precipitating ion is proportionately greater as the point of rapid coagulation is approached, since the lowering of the charge causes coalescence and agglomeration of the particles with a consequent decrease in specific surface. Above the point of rapid coagulation, the chloride is displaced from the coagulum by exchange adsorption without any marked decrease in specific surface and the curve follows the usual course of the adsorption isotherm.

3. Electrolytes with univalent precipitating ions which do not cause rapid coagulation in a critical zone, give chloride displacement curves which follow throughout the course of the adsorption isotherm as a result of exchange adsorption and gradual agglomeration.

4. The adsorption of anions by the positive sols tends to increase the adsorption of cations from the intermicellar solution and the agglomeration with decrease in specific surface which accompanies the lowering of the charge, tends to decrease the adsorption of both anions and cations. In the alumina sols investigated, the adsorbed $H^\cdot$ ion is in equilibrium with 10^{-4} to 10^{-5} mols per liter of $H^\cdot$ ion. The shifting of the adsorption equilibria which accompanies the addition to the sol of a salt of a strong acid and a strong base will increase slightly, decrease slightly, or leave unchanged the pH value depending on the relative magnitude of the two opposing tendencies. All of these cases have been realized experimentally. With salts such as $K_3C_6H_3O_7$ and $NH_4C_2H_3O_2$, buffer action always renders the pH value of the sol-electrolyte mixture somewhat higher than that of the original sol.

5. Ageing the freshly formed sol releases adsorbed $H^\cdot$ ion and the pH value falls off slightly. This is due to the loss of specific surface which accompanies the gradual agglomeration of the particles and the decrease in their hydrous character.

6. For the same equivalent concentration, the chloride displacing power and the coagulating power of the anions follows the same order which is: citrate > sulfate > oxalate > acetate > nitrate.

7. For the same equivalent concentrations the order in which the several salts increase the pH value on addition to the sols is: citrate > oxalate > acetate > nitrate > sulfate. At the precipitation value the order is: acetate > citrate, oxalate > nitrate > sulfate.

8. An adsorption mechanism has been outlined to explain the effect of the addition of electrolytes to the sol on the chloride displacement, the lowering of the charge, and the change in pH value.

9. The experimental results fail to justify the assumption that alumina sols formed by hydrolysis of $AlCl_3$ and dialysis are indefinite complex poly-ol basic aluminum chlorides of the Werner type and that the increase in pH value on adding salts such as KNO_3 and K_2SO_4 is due to displacement of (OH) groups which unite with $H^{\cdot}$ to form water. (Thomas) In one such sol the addition of K_2SO_4 decreased the pH value.

10. There appears to be no more justification for assuming that alumina sols formed by peptization of "grown" alumina with $AlCl_3$ are indefinite complex poly-ol basic aluminum chlorides than for assuming that AgCl sol formed by preferential adsorption of silver ion is a complex silver sub-chloride of indefinite composition.

11. A method has been described for the preparation of alumina sol with any desired chloride content from alumina formed by the interaction of amalgamated aluminum and water.

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HEAT OF WETTING OF CHARCOAL AS A MEASURE OF ITS ACTIVITY[1]

BY RUDOLPH MACY[2]

The use of charcoal as a gas adsorbent in the industry and in warfare has led to a voluminous literature on the methods of determining the quality of the charcoal. Probably the most complete bibliography on adsorption by charcoal is that included in the monograph on the subject by Blüh and Stark.[3] A typical discussion of the activity of charcoal is the recent article by Lowry[4] in which it is stated that most investigators use for their measure of activity of charcoal the "adsorptive capacity" of the charcoal under certain arbitrary conditions. In this category he includes the "retentivity" as defined by Chaney[5,6] and later explained more fully by Allmand[7].

The above mentioned paper by Lowry[4] contains a good resumé and bibliography of recent work on the relationship between activation of charcoal, the capacity of the charcoal, and its surface area. It is noteworthy, however, that practically nothing is to be found in any of the English or American journals on the usefulness of the heat of wetting of charcoal as a measure of activity.

A fairly complete historical account of investigations concerning heat of wetting is to be found in the text book by Freundlich.[8] The important names in this early work described by Freundlich are Pouillet (1823), Melsens (1874), Gore (1894), Chappuis (1883) and Gaudechon (1913). More recently, Berl and Andress[9] made a study of a precise method of determining adsorption isotherms of vapors on charcoal and followed this by determination of the heat of wetting in benzene. Their assembled data and curves show that the ether isotherms for various charcoals are practically quantitatively related to the heat of wetting in benzene. Berl and Andress consider the heat of wetting to be a function of both the "saturation capacity" and "intensity factor" of the adsorbent. Herbst[10] obtained the heat of wetting in water and in benzene and found that these data were proportional to the activity of the charcoal, when the activity is based on the adsorptive ability as compared with a standard high grade charcoal. Honig,[11] also, has shown that there is a distinct relation between heat of wetting and adsorptive capacity. Alekseyevskii[12] applied the methods of Berl and Andress (loc. cit.) to discover whether the heat effects could be used to grade the value of absorbent materials for a variety of vapors. Finally, Burstin and Winkler,[13] state that there is a direct proportionality between maximum adsorption of benzene vapor and heat of wetting in benzene.

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[1] Contribution from the Chemical Warfare Service, Edgewood Arsenal. This problem was suggested in June, 1929 by Captain M. E. Barker, Chief of Research Division, Chemical Warfare Service.

[2] Research Division, Edgewood Arsenal, Maryland.

[3] Blüh and Stark: "Die Adsorption" (1929).

[4] Lowry: J. Phys. Chem., **34**, 63 (1930).

[5] Chaney et al: Trans. Am. Inst. Chem. Eng., **15**, 283 (1923).

[6] Chaney: Trans. Am. Electrochem. Soc., **36**, 91 (1919).

[7] Allmand: J. Soc. Chem. Ind., **47**, 370 (1928).

[8] Freundlich: "Colloid and Capillary Chemistry."

[9] Berl and Andress: Z. angew. Chem., **34**, 369 (1921); **35**, 722 (1922).

[10] Herbst: Kolloid-Z., **38**, 320 (1926).

It is the purpose of this article to show that the heat of wetting in benzene is at once the most rapid and one of the best methods of determining the quality of a charcoal for gas adsorption. The heat of wetting is proportional not so much to the total adsorption capacity as stated by these earlier authors, as it is to the capacity for firmly held vapor, or retentivity. The distinction between these two capacities has been explained by Chaney (loc. cit.) as follows. Adsorption of vapor is due to two forces—

a) *Capillary, or physical, forces.* The vapor held by capillary adsorption practically has the properties of the liquid state, such as relatively high vapor pressure, and is easily eliminated either by application of vacuum or passage of dry air over the sample.

b) *Adsorptive, or chemical, forces.* Part of the vapor is held by secondary forces to the surface of the carbon. Its vapor pressure is extremely low and it can be completely eliminated only by heating. The amount of vapor held by true adsorption forces is the "retentivity."

Experimental Part

The charcoals used were of various types. A large number were obtained from commercial sources, and some were prepared at Edgewood Arsenal. The nature of the samples is described in Table II. The charcoal samples were dry-screened 8-14 mesh on Tyler Standard Screens, and in most cases they consisted of equal amounts of 8-10 and 10-14 mesh. The charcoal was dried for two hours at 150°C. before use.

The adsorption capacity, or saturation value, of the charcoal samples was determined in several ways. In all cases the capacity for benzene vapor was found by placing a weighed sample of two to five grams in a desiccator over the liquid. The temperature was that of the room and did not vary more than two degrees from an average of 25°C. The error introduced by this temperature variation was negligible considering the nature of the material being studied. Constancy in weight of the samples exposed to vapor was usually reached in about two days.

In one series of experiments the capacity of charcoal for chlorpicrin vapor was determined by the method just described for benzene, that is, by exposing weighed samples to the saturated vapor of chlorpicrin at 25°C. In another series of determinations the adsorption capacity of the charcoal was obtained at a chlorpicrin concentration in air of 47 mg./liter. This was done by passing the chlorpicrin-air mixture through a 10 cm. layer of the sample contained in a tube of 1.41 cm. diameter according to the usual procedure for measuring the service time of the charcoal. This method of determining service time has been discussed by Lamb, Wilson and Chaney.[14] After the service time had been obtained the passage of chlorpicrin through the charcoal sample at 25°C. was continued until the sample no longer gained weight. The total time required was usually less than two hours.

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[11] Honig: Kolloidchem. Beihefte, **22**, 345-420 (1926).

[12] Alekseyevskii: Zhurnal prikladnor Khimi (Moscow), **1**, 182 (1928).

[13] Burstin and Winkler: Przemysl Chem., **13**, 114 (1929).

The retentivity values were determined by placing the saturated charcoal samples in a U-tube of 1.4 cm. diameter and passing dry air through the sample at the rate of 1000 cm. per minute for two hours at 25°C. The amount of vapor retained at the end of this treatment was arbitrarily called the retentivity. Before using this method the retentivities had been measured by a method developed by Dr. Leo Finkelstein in this laboratory, by suspending the saturated samples in a bucket from a quartz fibre spring balance according to the procedure of McBain[15] and evacuating the system to about .002 mm. Hg at 25°C. The loss of weight was followed by a telescope and cathetometer arrangement and the system kept evacuated until no noticeable loss in weight occurred for about three hours. A single experiment occupied about 25 to 40 hours, but practically the same results were obtained by passing dry air over the sample for two hours as already described, and the data were also more consistent and more easily duplicated by the latter rapid method.

As already stated, the retentivities obtained in this work are arbitrary values in that they are measured by weighing the retained vapor after air has been passed over the sample for exactly two hours. In Fig. 3 a set of curves is given which show the rate of loss of vapor under these arbitrary conditions. In two hours all the charcoals give up the loosely held vapor, and then begin to give up the remainder at a slow rate which is nearly the same for all the samples. The two hours desorption period therefore should furnish good relative retentivity values, even though the results obtained are arbitrary ones.

The apparatus required to determine the heat of wetting was found to be very simple. The usual practice in measuring the heat effect when a solid is immersed in a liquid is to use a well insulated reaction vessel, the most common apparatus for such a purpose being a Dewar flask. The preliminary experiments on heat of wetting of charcoal were accordingly made in a 200 cc. Dewar flask, fitted with a Beckmann thermometer and a glass stirrer both of which passed through a rubber stopper to prevent evaporation of the liquid. Measurements made in this way were very accurate, but tedious, and would not be appropriate for the use of routine analysis in plant control work. In order to keep all such heat measurements comparable it is necessary to start each experiment at some common temperature such as 25°C., since the specific heats vary with temperature. Temperature changes in a vacuum flask are so slow that each time fresh materials are placed in the flask a considerable period must elapse before the actual determination can be made.

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[14] Lamb, Wilson, and Chaney: J. Ind. Eng. Chem., **11**, 420 (1919).

[15] McBain and Bakr: J. Am. Chem. Soc., **48**, 690 (1926).

Although the heat of wetting measurements should begin at some common temperature, this fixed point can vary several degrees without having an appreciable effect on the results obtained. Furthermore, the heat of wetting determination with charcoal is very rapid, the maximum temperature rise when it is wetted being reached often in 30 seconds. Heat transfer to surroundings are therefore very slight. All that is necessary then is to use a test tube for the reaction vessel with an outer test tube to serve as an air-jacket, assembled as in an ordinary freezing-point determination. When a fresh supply of liquid at room temperature is placed in such an apparatus only a few moments elapse before it reaches a fairly constant temperature which will not be far from that of the room and can be taken as the initial temperature of the experiment. The room in which the present work was conducted seldom varied more than 2° from an average of 25°C.

The Beckmann thermometer had to be dispensed with, since it would necessitate starting each measurement at a predetermined fixed temperature, whereas it is more convenient to begin the heat measurement at whatever the temperature in the test tube might be, within a limit of 2 to 3 degrees. In its place a thermometer graduated to 0.02°C. was used, reading from 17° to 31°C.

Benzene was chosen as the wetting liquid after a study of the adsorption curves for several vapors on charcoal showed that it is one of the most highly adsorbed substances. It would therefore be reasonable to suppose that the heat effects would be comparable with other determinations on charcoal in which high adsorptive capacity is a predominant feature. Such tests are the accelerated chlorpicrin tube test, and retentivity. The volumes of charcoal and of benzene used were simply those found by trial to be most convenient in the apparatus employed. The apparatus used can be found in any laboratory. The following method of carrying out the test has been found to be satisfactory.

After pouring 20 cc. of benzene into the tube, the thermometer and stirrer were inserted and the contents stirred a few moments until the temperature was constant, and the temperature recorded to 0.01°C.

About 5 cc. of charcoal was weighed out to 0.001 g. in a slender weighing tube about 1/2 inch in diameter. The thermometer and stopper were partially lifted from the tube, leaving the stirrer loop resting at the bottom, and the charcoal was poured in rapidly. The stopper and thermometer were replaced and then on the first up-stroke of the stirrer the charcoal and benzene were well mixed. Stirring was continued vigorously, the mercury thread climbing rapidly to a maximum position. A little practice is necessary before duplicate results can be obtained. An active charcoal gives a very rapid rise (the maximum reached in less than 30 seconds); less active charcoals are characterized by a slower rise and slower fall in temperature. The maximum rise in temperature is recorded to 0.01°C. After a determination the test tube is rapidly dried by a stream of compressed air. From the weight of sample and rise in temperature the heat of wetting is calculated in °C./g. The apparent density is determined separately, and the heat of wetting is then calculated in °C./cc.

The heat capacity of the apparatus and its contents was calculated from the standard physical constants of its components, assuming an average specific heat for charcoal of 0.2 and an average weight for the sample of 2.0 grams. The water equivalent was found to be almost exactly 10.0, so that it was only necessary to multiply the heat of wetting data by the factor 10 in order to convert it to calories per g. or per cc. of charcoal. This factor is not strictly accurate because of variations in the weight of sample and specific heat of different charcoals.

Summary and Discussion of Results

Heat of Wetting and Particle Size. The effect of the size of the charcoal granules was studied, using a high grade commercial coconut charcoal. This was screened to give fractions with the mesh sizes listed in the following summary:

Mesh	Apparent Density	Sample g.	Heat of Wetting °C./g.	°C./cc.	cal./cc.	cal./g.
6-8	.487	2 318	1 88	0.915	9.15	18.8
8-10	.47	2.257	2.13	1.00	10.0	21.3
10-14	.465	2.322	2.18	1.01	10.1	21.8
14-20	.455	1.827	2.15	0.98	9.8	21.5

Within the range of particle sizes usually employed, that is, 8 to 20 mesh, the variation in size has practically no effect on heat of wetting.

Relation between Heat of Wetting in Benzene, and the Maximum Adsorption and Retentivity of Benzene

The relations between these quantities are shown graphically in Figs. 1 and 2, and the data are presented in Table I. Burstin and Winkler (loc. cit.) claim that the relation between total adsorption of benzene vapor and heat of wetting in benzene is expressed by a straight-line function A = K Q, where

A is maximum adsorption in percent by weight

Q is heat of wetting in calories per gram

K is a constant, equal to 1.9 percent calories (A being expressed in parts adsorbed per 100 parts of charcoal).

A careful study of their paper indicates that they did not use more than two different commercial samples of charcoal (one made by Bayer and the other by Merck) and these were both of similar characteristics. The work reported in this article, however, is based on a wide variety of types, as shown in Table II.

In Fig. 1 the data have been plotted to agree with the system of units employed by Burstin and Winkler, the broken line representing the constant K as evaluated by these authors. In Fig. 2 the data are given on the more usual volume basis. In both diagrams it is clear that the data are more accurately represented by smooth curves rather than by straight lines, and this is also evident for the corresponding chlorpicrin results shown in Figs. 4 and 5.

Inspection of Figs. 1 and 2 proves beyond doubt that the heat of wetting is a function of the retentivity of the charcoal rather than of its adsorption capacity. This to be expected from the very nature of the experiment. The heat evolved when charcoal is wetted by liquid benzene is due to some surface phenomenon—whether it is considered to be an initial formation of a monomolecular layer or condensation in capillaries of molecular size, or both, is immaterial. It is hardly likely that penetration of the larger capillaries by the liquid would give rise to heat effects of measurable magnitude, since it is simply a sponge effect and not true adsorption.

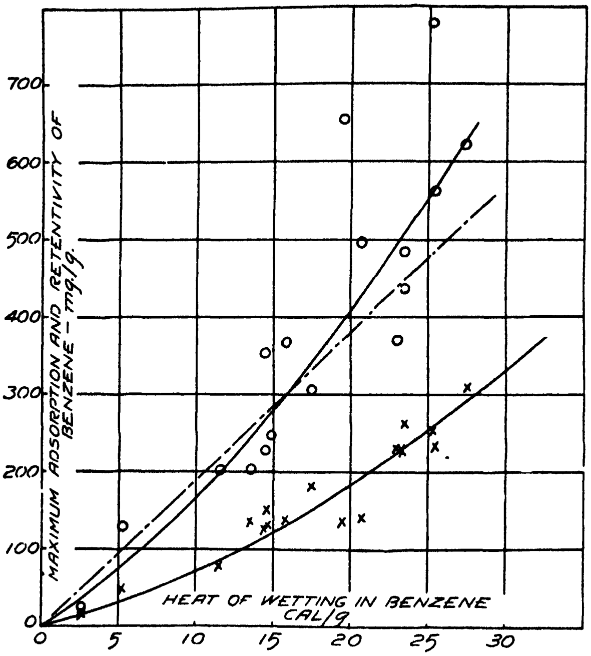

Fig. 1

Adsorption data—circles; retentivity data—crosses.

Thus, the Urbain charcoal and the sample of German charcoal in Table I have very high saturation capacities (this is more readily appreciated from Fig. 2) but these saturation values are out of proportion with their corresponding heat effects. At saturation they probably store up considerable benzene vapor in large capillaries in practically the liquid state. This excess vapor is easily lost, as shown in Fig. 3, when dry air is passed over the charcoal. The amount of vapor firmly held by Urbain and the German charcoal is, however, accurately predicted by the heat of wetting.

It is a logical conclusion, therefore, that the heat of wetting is a measure of the amount of vapor held by true adsorption forces, or retentivity.

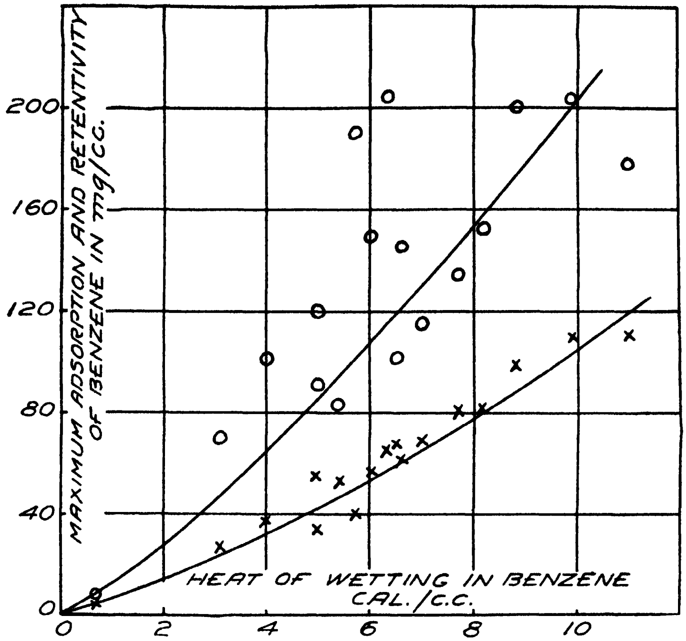

FIG. 2

Adsorption data—circles; retentivity data—crosses.

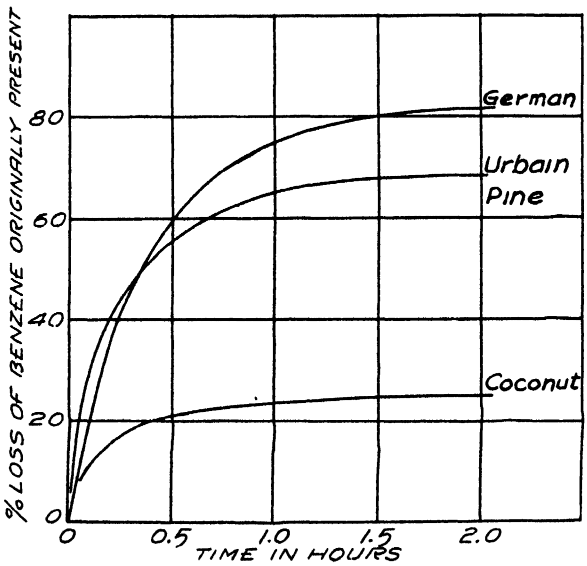

FIG. 3

Rate of loss of adsorbed benzene by charcoal in a current of dry air.

Tryhorn and Wyatt[16] found that a discontinuity occurs in the rate of adsorption of benzene vapor by a coconut charcoal when it has adsorbed 120 × 10^5 moles per gram, and that its total saturation is 204 × 10^5 moles. The break in the curve was ascribed to the sudden formation of a liquid layer. The ratio 120/204 is nearly identical with the ratio of the retentivity and saturation data given in Table I for the coconut charcoal. This confirms the assumption that the retentivity value is a measure of the adsorbed vapor which is held firmly by secondary valence bonds, while the part that is loosely held has properties corresponding to the liquid state.

TABLE I

Relation between Heat of Wetting in Benzene, Maximum Adsorption of Saturated Benzene Vapor, and Retentivity of Benzene at 25°C.

	Sample and Number	Apparent Density	Heat of Wetting		Maximum Adsorption		Retentivity	
			cal./g.	cal./cc.	mg./g.	mg./cc.	mg./g.	mg./cc.
124	Tec-Char	.29	2.4	0.7	26	7	14	4
125	Norit	.19	15.8	3.1	367	70	137	26
108	Batchite	.78	5.1	4.0	129	101	48	37
61	Pine	.24	20.8	5.0	496	120	142	34
56	Oak	.44	11.4	5.0	206	91	128	56
24A	Ironwood	.40	13.5	5.4	206	83	135	54
120	German	.29	19.6	5.7	655	190	136	40
107	Coal Briquets	.42	14.3	6.0	354	149	135	57
101	Urbain	.25	25.2	6.3	780	203	258	65
23	Ironwood	.45	14.5	6.5	227	102	150	68
39	Maple	.26	25.4	6.6	560	146	234	61
126B	Oak	.44	17.5	7.7	307	135	184	81
15A	Ironwood	.47	14.9	7.0	244	115	148	70
38	Oak	.35	23.4	8.2	437	153	233	82
50B	Oak	.32	27.5	8.8	623	200	310	99
51A	Oak	.42	23.6	9.9	486	204	263	110
102	Coconut	.48	23.0	11.0	371	178	231	111

TABLE II

Nature of Charcoals listed in Table I and Figs. 4 and 5

Name	Description
Tec-Char	—A wood charcoal made by the Tennessee Eastman Corporation. Serial No. K-200.
Norit	—A commercial decolorizing charcoal made from wood.
Batchite	—The generic name for steam activated anthracite coal.
Pine	—Made by carbon dioxide activation of yellow pine.
Oak	—Made by carbon dioxide activation of oak.

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[16] Tryhorn and Wyatt: Trans. Faraday Soc., 22, 134 (1926).

TABLE II (Continued)

Nature of Charcoals listed in Table I and Figs. 4 and 5

Name	Description
Maple	—Made by carbon dioxide activation of maple.
Ironwood	—Made by carbon dioxide activation of ironwood.
Coconut	—Made by steam activation of coconut shells. Commercial samples were obtained from: Barneby-Cheney Engineering Co., Columbus, Ohio. National Carbon Company, Cleveland, Ohio. Carbide and Carbon Chem. Corporation, New York
German	—From a German world-war canister; probably made by zinc chloride impregnation and subsequent activation of wood
Coal Briquets	—Made from a mixture of hard and soft coals, steam activated.
Urbain	—Briquetted lignite coke, made by the Urbain Corporation of Niagara Falls, N. Y.
Lamp Black	—Made by steam activation of lamp black briquetted with a sugar binder.
Aqua Dag Graphite	—Made by neutralizing Acheson's Aqua Dag, filtering, washing, drying, and crushing to 8-14 mesh.

Relation between Heat of Wetting in Benzene, and the Maximum Adsorption and Retentivity of Chlorpicrin Vapor

The discussion of these three factors leads to exactly the same conclusions which have been expressed in the preceding section, that is, the heat of wetting of charcoal is proportional more to its retentive capacity than its adsorptive capacity. The data obtained on the adsorption and retentivity of chlorpicrin are so numerous that it was not thought advisable to use up space by a tabulation of the results when they could be adequately represented diagrammatically. Most of the data obtained are shown in Fig. 4 and Fig. 5, all the results being plotted on a volume basis.

The adsorption capacities in Fig. 4 were all obtained by exposing the samples to saturated chlorpicrin vapor at 25°C. In many cases the capacity was measured in a stream of chlorpicrin vapor, as described in the experimental part; the results obtained showed that condensation of liquid chlorpicrin on the charcoal in saturated vapor probably did not take place since the relative capacities obtained were proportional to the concentration.

In Figs. 4 and 5 the average curves drawn were influenced principally by the data for coconut charcoal since that is the standard type by which the quality of other charcoals is judged. The most striking proof that heat of wetting is a function of retentivity and not of capacity is given by the data on a sample of Acheson Aqua Dag, which is really not a charcoal but a high grade of graphite. The material had been treated as described in Table II.

The heat of wetting of this graphite was very small, yet it had an adsorption capacity equal to that of a fairly good coconut charcoal. Its retentivity, on the other hand, was practically zero, in agreement with the heat of wetting.

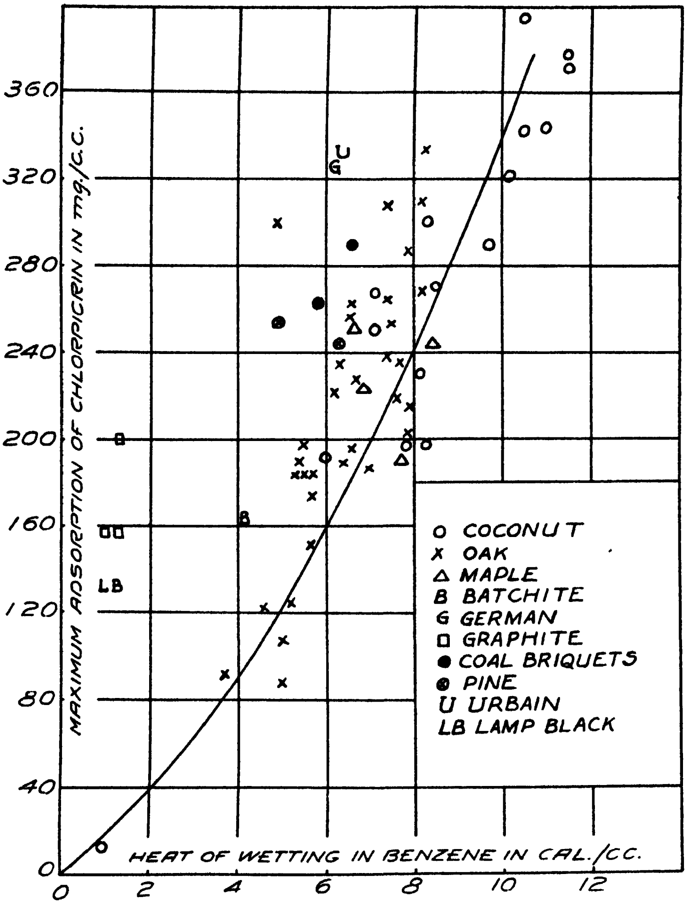

FIG. 4
Relation between heat of wetting in benzene and maximum adsorption of saturated chlorpicrin at 25°C.

Relation between Heat of Wetting and Surface Area of Charcoal

The data presented in this paper show that there is a proportionality between the heat of wetting of charcoal and its retentive capacity. In Chaney's[5,6] definition of retentivity there is the implied assumption that the retentivity of charcoal is determined by the extent of its surface. This idea appears to have a fairly wide acceptance. If this is true then the heat of wetting is a measure of the available surface of the charcoal as well as the retentive capacity. While this article was being written for publication, two other papers have appeared in which the authors also express the opinion that heat of wetting is a function of surface area.

Berl and Burkhardt[17] measured the heat of wetting of a series of activated charcoals, and also measured the adsorption of methylene blue from solution according to the procedure of Paneth and Radu.[18] According to the latter authors methylene blue probably forms a monomolecular film on charcoal and can be used to estimate the surface area of the adsorbent. The heat of wetting and methylene blue adsorption were found to be roughly equivalent; a heat of wetting of 1°C. produced by 1.5 g. of charcoal and 10 cc. of benzene is proportional to a surface area of 60 square meters per gram.

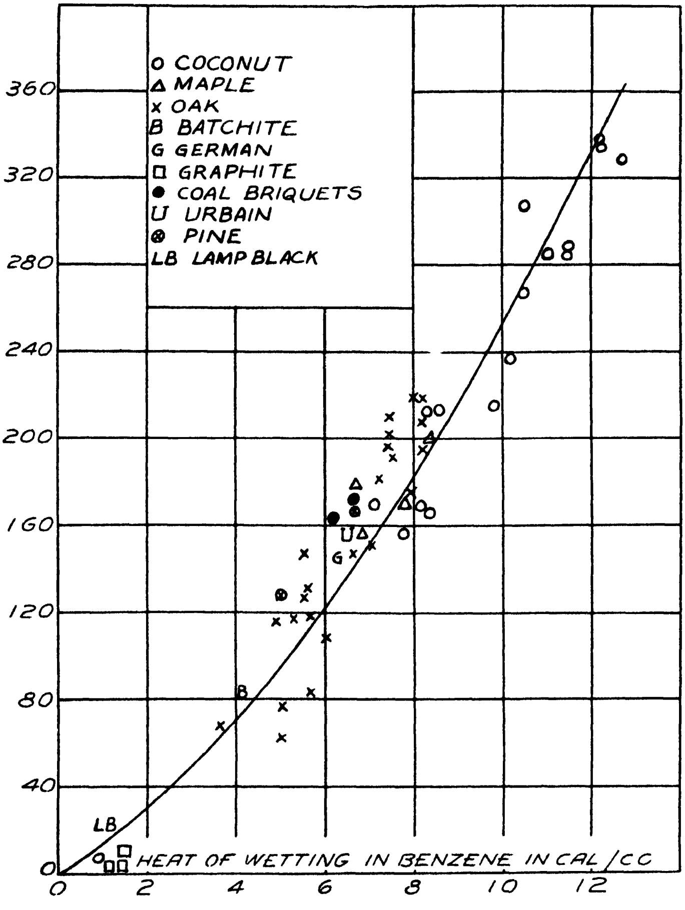

FIG. 5

Relation between heat of wetting in benzene and retentivity of chlorpicrin at 25°C.

Bartell and Fu[19] have made a study of the various methods of measuring the surface area of charcoal and silica gel, and showed that the surface area can be calculated from heat of wetting and adhesion tension. "This method of determining surface area does not depend on the measurement of adsorption from solution; it is, therefore, free from those uncertainties which arise from the use of doubtful assumptions concerning the shape and dimensions of the adsorbed molecules, and the unknown thickness of the adsorbed layers." They obtained a value of 635 square meters for the specific surface of charcoal, which is higher than most values recorded in the literature.

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[17] Berl and Burkhardt: Z. angew. Chem., **43**, 330 (1930).

[18] Paneth and Radu: Ber., **57**, 1221 (1924).

[19] Bartell and Ying Fu: Colloid Symposium Annual, **7**, 135.

When the above values published by Berl and Burkhardt are recalculated to the same basis on which the heat of wetting was determined in the present work, it is found that a heat of wetting of 1°C. per gram of charcoal is equivalent to a specific surface of 180 square meters. This is in good agreement with the value of 200 square meters calculated from the following data for a high grade commercial coconut charcoal. The calculation is based on the assumption that chlorpicrin retentivity is a measure of the amount covering the charcoal in a monomolecular layer:

Heat of wetting = 2.64°C./g. in 20 cc. of benzene.
Chlorpicrin Retentivity = 330 mg./cc. = 718 mg./g.
Cross-Section Area of Chlorpicrin Molecule = 20 square Ångstrom units (an average figure for molecules in thin films given by Adam, International Critical Tables 4, 476).
Area covered by chlorpicrin = 528 sq. m./g. of charcoal.
Heat of wetting of 1°C./g. is equivalent to 200 sq. m./g.

The above sample of coconut charcoal is one of the best obtainable commercially. Its specific surface area of 528 sq. m. is in fairly good agreement with that found by Bartell and Fu for a sugar charcoal, and the proportionality between heat of wetting and specific surface area is in good agreement with the above-mentioned finding of Berl and Burkhardt. In Table I about six charcoal samples will be found which have a heat of wetting on a weight basis close to that of the above sample of coconut charcoal; these samples include oak, Urbain, and maple charcoals. The heat of wetting in cal./g. in Table I should be divided by 10 to give the corresponding °C./g. values. On a volume basis, however, these charcoals are not so good as the coconut.

Before concluding, it is desired to point out an important factor which has not yet been touched on in this discussion. In the course of this work, after much experience in the manipulation of the apparatus had been acquired, it was found that some charcoals when poured into benzene caused a much more rapid rise in temperature than others. The more active charcoal in this respect usually was found to be better in all other respects. In several cases the time required for the total rise in temperature after mixing was noted with a stop-watch; the following experiment is typical:

Charcoal	Sample cc.	Rise in Temperature Time Sec.	°C.	°C./cc.	Heat of Wetting °C./cc.	Chlorpicrin Retentivity mg./cc.
20 Oak	5.35	21.4	2.66	0.023	0.50	76
43Ab Oak	5.00	14.0	2.46	0.035	0.49	115

These two samples with the same heat of wetting show a much different activity when dropped into the benzene, and the sample which produces a more rapid evolution of heat also has a higher retentive capacity. This and a few similar experiments may be explained by the assumption that the heat of wetting measures the surface area of the charcoal but not the activity of the surface. This explanation is in accord with a statement of Lamb and Coolidge[20] who found that "the heats of adsorption of vapors are very nearly the same on inactive as on active charcoals of the same kind." This is equivalent to stating that the activity of the surface does not affect the total evolution of heat when vapors are adsorbed by charcoal. Unfortunately, further work on this problem was discontinued before the results obtained were sufficient to give any definite conclusions.

Conclusions

The literature has been reviewed on the determination of the heat of wetting of charcoal. Data are presented which agree with statements of other authors that the heat of wetting in benzene is a good rapid test of the value of charcoal as a gas adsorbent. However, it is shown that the heat of wetting is not a function of the adsorption capacity of charcoal, but of the capacity for firmly held vapor, or retentivity. It is probable that the heat of wetting in benzene, and the retentivity of adsorbed vapor, are a measure of the surface area of charcoal.

Edgewood Arsenal,
Edgewood, Md.
August 1, 1930.

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[20] Lamb and Coolidge: J. Am. Chem. Soc., **42**, 1146 (1920).

STUDIES IN THE SOLUBILITIES OF THE SOLUBLE ELECTROLYTES

V. An Estimation of the Radii of Ions in Saturated Solutions

BY ARTHUR F. SCOTT

For any given temperature the apparent molal volume φ of a salt in a saturated solution containing one mol of salt is defined by the expression

$$\varphi = V - Nv_1 \qquad (1)$$

where V is the volume of the solution; N is the number of mols of water in the solution; and v_1 is the volume of one mol of pure water.

In a previous paper[1] it was shown that for extremely soluble salts the following relationship between φ and N is presumably valid:

$$\varphi = aN^2 + b \qquad (2)$$

The constants a and b are characteristic of each salt. The latter constant b is particularly important because it is the apparent molal volume of the salt when no water is present. Moreover, if the change in φ with temperature is regarded as the consequence only of a change in the volume of the water present in the saturated solution. b may be looked upon as the volume of the ions of a salt in the saturated solution. In the paper already referred to values of b were calculated for eight alkali salts and in magnitude they were found to be larger than the space occupied by the ions in a crystal lattice and smaller than the effective volumes of the ions in dilute solutions. In the present article these considerations have been extended to permit an estimation of the radii of the individual ions. Such an estimation appears possible by making use of a new empirical relationship from which can be calculated the limiting volume $\bar{v}$ which contains the ions of volume b Since the ratio $b/\bar{v}$ is of the order of magnitude found for the crystalline state, we can, by assuming that the ions are arranged in a specific lattice, compute definite values for the radii of the ions.

We shall first consider the following empirical relationship between V and N at the same temperature:

$$V^{2/3} = \alpha N + \beta \qquad (3)$$

In order to test this relationship Fig. 1 has been constructed by plotting the experimental data for eight alkali salts. The essential data for this graph are collected in Table I. An examination of Fig. 1 shows that the plotted points for each salt, with very few exceptions, fall directly on a straight line. This method of plotting is, however, not very sensitive to experimental errors in the basic density and solubility measurements. Errors in density measurements will affect only the $V^{2/3}$ term but, since they are much smaller than errors

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[1] Scott and Durham: J. Phys. Chem., **34**, 2035 (1930).

TABLE I

$V^{2/3}$ and N Values of Salts at Different Temperatures (Fig. 1)

Temp. °C.	CsCl[1] $V^{2/3}$	CsCl[1] N	RbCl[1] $V^{2/3}$	RbCl[1] N	$NaNO_3$[1] $V^{2/3}$	$NaNO_3$[1] N
0	27.9	5.76	33.4	8.73	28.07	6.45
20	26.4	5.01	30.7	7.36	25.83	5.36
40	25.3	4.49	28.9	6.47	23.98	4.50
60	24.5	4.08	27.6	5.81	22.41	3.79
80	23.8	3.74	26.5	5.27	21.08	3.20
100	23.2	3.45	25.7	4.84	19.85	2.68

Temp. °C.	NaBr[2] $V^{2/3}$	NaBr[2] N	NaI[2] $V^{2/3}$	NaI[2] N	KBr[2] $V^{2/3}$	KBr[2] N	KI[2] $V^{2/3}$	KI[2] N
0	28.82	7.13	25.78	5.20	40.35	12.23	31.56	7.19
25	26.66	6.04	24.42	4.53	35.63	9.68	29.65	6.21
35	25.69	5.60	23.76	4.22	34.25	8.91	29.00	5.84
45	24.67	5.14	—	—	—	—	—	—
50	24.16	4.91	22.50	3.67	32.70	8.09	28.25	5.45
60	24.11	4.85	—	—	—	—	—	—
63	—	—	21.20	3.09	—	—	—	—
68	—	—	20.51	2.81	—	—	—	—
75	24.10	4.78	20.53	2.80	—	—	—	—
92	24.05	4.71	20.56	2.77	29.70	6.51	26.69	4.63

KCl[3]

Temp.	19.6	25[4]	50.0[2]	59.9	68.0[2]	74.8	89.5	92.0[2]	108.1
$V^{2/3}$	39.50	38.58	35.17	33.98	33.35	32.69	31.58	31.49	27.68
N	12.04	11.53	9.68	9.03	8.70	8.35	7.75	7.71	5.66

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[1] International Critical Tables.

[2] Scott and Durham: J. Phys. Chem., **34**, 1424 (1930).

[3] Berkeley: Phil. Trans, **203A**, 189 (1904).

[4] Scott and Frazier: J. Phys. Chem., **31**, 459 (1927).

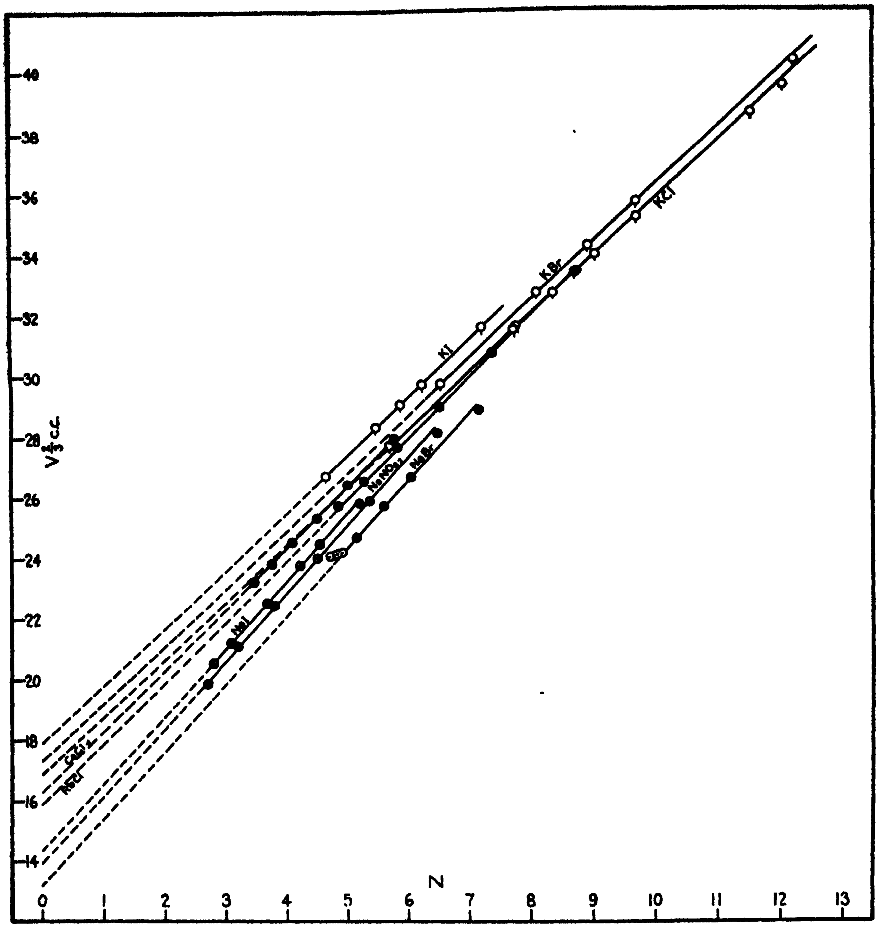

FIG. 1
The Variation of the Volume of a Saturated Solution with its Water Content N.

in solubility measurements, they are probably negligible. Errors in the determination of solubility affect both terms, the value of N somewhat more than the corresponding value of $V^{2/3}$. The few cases in which the plotted points do not fall on the line could all be attributed to errors in the solubility measurements. Nevertheless, until more data are available this means of testing the empirical relationship can not be regarded as decisive.

Indirect evidence in support of the plausibility of equation (3) is to be found by differentiating it with respect to N, as below:

$$\frac{dV}{dN} = \frac{3}{2}\,\alpha V^{1/3} \tag{4}$$

If we take the $V^{1/3}$ term to represent the average distance between the ions in a saturated solution, the expression means that the change in volume with N is directly proportional to the separation of the ions. This result is qualitatively what would be expected on the assumptions of the electrostriction theory. If water (N) is added to a saturated solution in which the ions are relatively close, the added water will necessarily come into a region where the ionic forces are stronger and will consequently be more compressed than would be the case if the ions were farther apart. The increase in volume of the solution upon addition of water would be less in the first case than in the second. It is also noteworthy that the constant α turns out to be identical for certain salts, a fact which can be taken to mean that in saturated solutions of these salts the effect of the ions on the water molecules is essentially the same. If the salts of one group are considered, it is seen that they have in common one ion which is relatively stronger and which may be looked upon as the ion influencing the change in volume of the water molecules. In other words we have an additional example of a possible dominant ion effect.[1] Attention should also be directed to the fact that a change in the solid phase is marked by a discontinuity in the linear relationship. For example, in Fig. 1 a dotted line is drawn to indicate the variation of $V^{2/3}$ with N for sodium bromide above the transition temperature. It is at once apparent that the constants of this line (equation 3) are altogether different from those of the solid line, which correspond to the hydrated salt.

TABLE II

Values of β and Related Quantities

	NaBr	$NaNO_3$	NaI	RbCl	CsCl	KCl	KBr	KI
β	13.2	13.9	14.3	15.9	16.3	16.9	17.3	17.9
$\bar{v}$	48.0	51.8	54.1	63.4	65.8	69.5	72.0	75.7
b	31.4	39.2	42.8	40.4	48.4	34.3	41.6	54.7
ψ	0.65	0.76	0.79	0.64	0.74	0.49	0.58	0.72

For our purpose the constant β is particularly important and the values taken from Fig. 1 are given in Table II. In the same table are likewise given figures for $\bar{v}$, which is equal to $\beta^{3/2}$. The quantity $\bar{v}$ is the hypothetical, limiting volume in which one mol of salt is contained when it is in the same state as in a saturated solution but when no water is present. The corresponding values of b (equation 2), which is the space occupied by the ions of an electrolyte under the above conditions, are also presented in Table II and are taken from the paper already mentioned. Finally, we shall find it convenient to introduce the quantity $\psi = b/\bar{v}$ which is termed the space-filling quotient. The values of ψ given in Table II accordingly indicate the fraction of $\bar{v}$ which is occupied by the ions (b).

It will be observed that, although the ψ values vary widely among themselves, they are essentially greater than 0.5. This fact permits[2] the preliminary deduction that the ions in volume $\bar{v}$ must be packed rather closely, in a manner similar to that of ions in a crystalline solid. For any mode of packing the quotient ψ will vary with the ratio r_1/r_2 of the radii (r_1 and r_2) of the two ions involved. This variation, when the ions are assumed to be perfect spheres, is shown by the two solid lines drawn in Fig. 2. The line marked C.N. = 8 is for the cesium chloride structure where the co-ordination number is eight; the line marked C.N. = 6 is for the simple rock-salt structure. The value of ψ for a tetrahedral mode of packing (C.N. = 4) is indicated only for the one case where the radii ratio equals unity. Furthermore, the extreme limits of the drawn lines are established by the minimum permissible values of the radii ratios.[1] The conditions which determine these minimum values are (1) any sphere (ion) of one sort must be in contact with the number of adjacent spheres (ions) of the second sort given by the co-ordination number and (2) the adjacent spheres must not intersect.

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[1] Scott: J. Phys. Chem., **33**, 1000 (1929).

[2] R. Lorenz: "Raumerfüllung und Ionenbeweglichkeit," page 38.

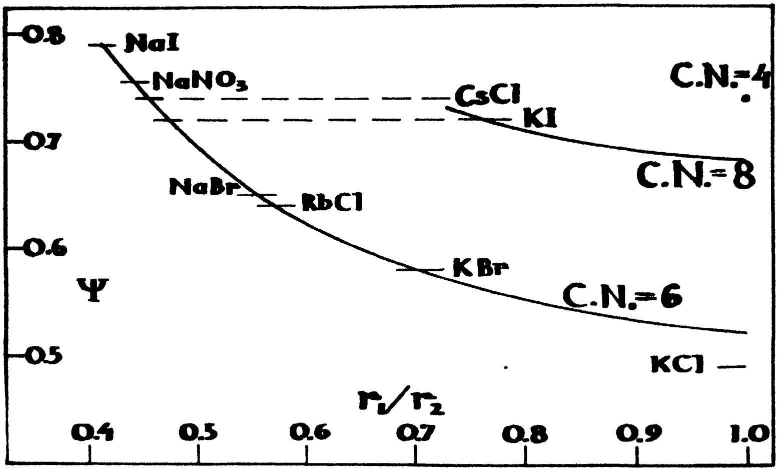

FIG. 2
Variation of Ψ with ratio of ionic radii.

In Fig. 2 are marked the ψ values (Table II) of the different salts. With the exception of the value of potassium chloride the indicated ψ values can be plotted on the C.N. = 6 curve. On the other hand only two salts, potassium iodide and cesium chloride, have ψ values which can also be plotted on the curve drawn for the cesium chloride structure. In considering the significance to be attached to this graph it is important to keep in mind the two assumptions which are involved: first, the domain of the ions is spherical; and second, the oppositely charged ions are in contact. Since the values of b and $\bar{v}$, obtained by extrapolation, are for indeterminate temperatures above 100°C., the above two assumptions are only approximately valid. If, however, we continue to take b to be independent of temperature, a correction for the effect of temperature on $\bar{v}$ would tend to increase the magnitude of ψ. Such a correction, for example, would bring the ψ value of potassium chloride nearer to the drawn curve; but the same correction applied to the ψ value of sodium iodide would make it too large. Although no estimation of the magnitude of this temperature correction can be made, one conclusion is worth noting: the effect of a temperature correction will be to decrease the radii ratio, that is, to increase the disparity between the radii of the constituent ions.

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[1] Goldschmidt: "Crystal Structure and Chemical Constitution," The Faraday Society, (1929).

With the values of b and $\bar{v}$ at hand it is possible to compute the radii, r_1 and r_2, of the ions constituting each salt by means of the following equations:

$$(r_1 + r_2)^3 = A\,\bar{v}$$

$$N\frac{4}{3}\pi\,(r_1^3 + r_2^3) = b$$

Here N is Avogadro's number; A is a constant dependent on the type of crystal structure. For rock-salt structure it has the value 0.938×10^{-8} and for cesium chloride structure its value is 1.02×10^{-8}. The values of r_1 and r_2 obtained by solving these equations, using the $\bar{v}$ and b values contained in Table II, are given in Table III. The radii ratios given in the bottom row are, of course, identical with those which would be obtained from the curves drawn in Fig. 2 by using the appropriate values of ψ. Only for the two possible cases, cesium chloride and potassium iodide, have the radii been calculated for the two types of crystal structure. No values for the radii of the ions in the case of potassium chloride are presented because the solution of the two equations yields imaginary values. This fact means merely, as has already been pointed out, that the oppositely charged ions are not in contact.

TABLE III

Radii of Ions in the Limiting, Hypothetical State

Salt	NaBr	$NaNO_3$	NaI	RbCl	CsCl		KBr	KI	
Structure	NaCl	NaCl	NaCl	NaCl	NaCl	CsCl	NaCl	NaCl	CsCl
$r_1 \times 10^{-8}$cm.	1.21	1.07	1.04	1.37	1.20	1.73	1.59	1.28	1.85
$r_2 \times 10^{-8}$cm.	2.20	2.43	2.51	2.37	2.59	2.40	2.31	2.69	2.47
r_1/r_2	0.55	0.44	0.41	0.58	0.46	0.72	0.69	0.48	0.75

It is of considerable interest to compare these values of the ionic radii with the values obtained in other ways. Although we have no means of knowing which of the two ions is the anion, we shall assume that the one (r_2) with the larger radius is always the anion. The reasonableness of this assumption rests on the fact that practically every estimate of the relative magnitudes of the cations and anions under consideration indicates that the anion is larger than the cations. The values of r_1 and r_2, interpreted according to the above assumption, are plotted in Fig. 3: those values involving the assumption of a rock-salt structure are plotted as circles while those involving the assumption of cesium chloride structure are plotted as triangles. The salt from which each value is derived is also given. As a basis of comparison the ionic radii found by Goldschmidt[1] (line A) and by Webb[2] (line B) are shown in the figure.

The values of the ionic radii portrayed by line A are those found for the ions in crystals; they are in excellent agreement with the values calculated

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[1] Goldschmidt: "Crystal Structure and Chemical Constitution." The Faraday Society, page 282 (1929).

[2] Webb: J. Am. Chem. Soc., **48**, 2589 (1926).

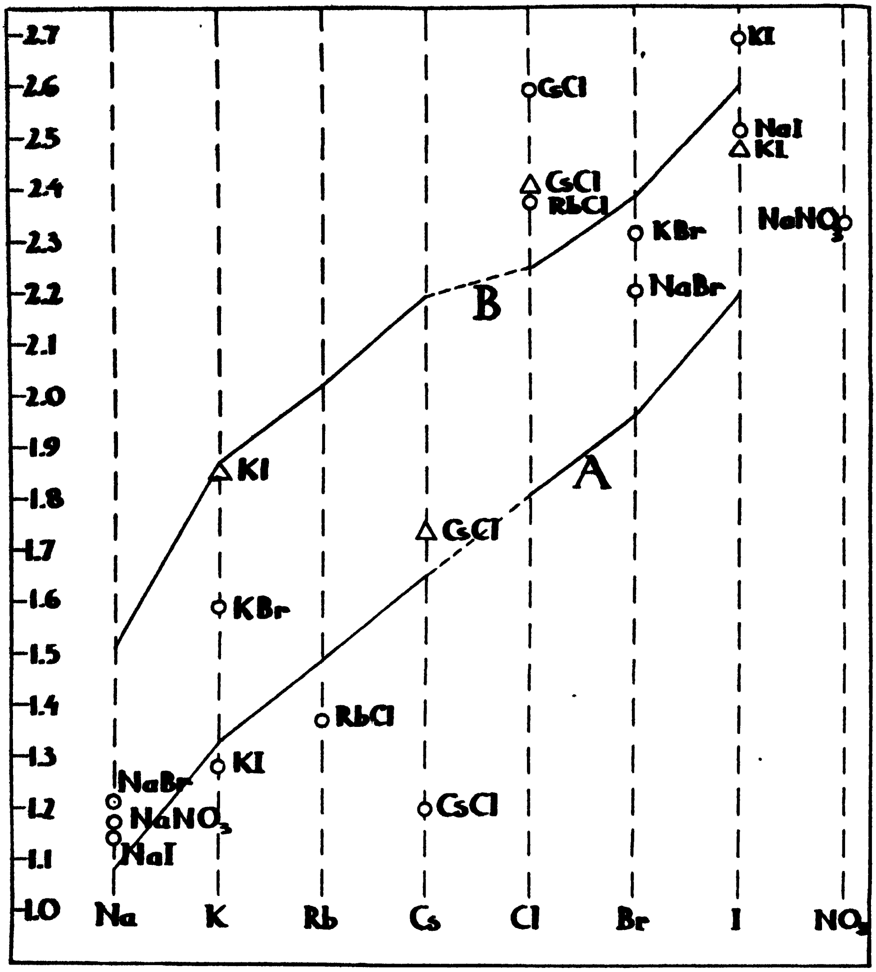

Fig. 3
Calculated radii of ions in Ångstrom units.

from the theory of wave mechanics and with those deduced from the optical data of the crystalline salts. The ionic radii which determine line B are the effective radii of ions invery dilute solutions, calculated from the theory of electrostriction. The effective radius of an ion is understood to be "the radius of a sphere surrounding the center of an ion, inside which there are no water molecules." We may therefore look upon these effective radii as the apparent radii when the ions are in the same state as in very dilute solution but when no water is present. They would thus be comparable to the apparent radii obtained in this paper, provided that the effective volumes do not undergo a change with concentration.

The plotted points in Fig. 3 appear to fall into two distinct groups: the anions have radii approximately the same as the effective radii calculated by Webb; the cations have dimensions very close to those found for the same ions in crystals. This generalization is strengthened by the observation made with respect to the temperature correction, namely, that such a correction would act to increase the ratios of the ionic radii. In other words, a temperature correction would affect the calculated radii in such a way as to emphasize the division of the cations and anions into two groups. Since we have postulated that b is the volume of the salt-ions in the saturated solution, we must regard the calculated radii as approximately the effective radii of the ions in the saturated state. On the ground of this analysis it is allowable to suggest that concentration has no influence on the effective volume of anions whereas it does bring about a diminution of the effective volume of the cation.

The foregoing interpretation is, of course, only tentative because of the limited data on which it is based. A further difficulty in the way of drawing a definite conclusion is the necessity of assuming a specific mode of packing of the ions in the limiting state. An illustration of this difficulty is the case of potassium iodide. Although the face-centered structure (C.N. = 6), which is the structure of this salt in the crystalline state, gives results which agree excellently with the above interpretation, the body-centered structure (C.N. = 8), which is equally possible, gives a quite contrary result. In the latter case, as can be seen in Fig. 3, both ions have radii corresponding to those found by Webb. In this connection it is worth noting that the assumption of a body-centered structure for cesium chloride, which is the normal crystalline structure, yields reasonable figures for the ionic radii, whereas the assumption of the other structure yields abnormal, almost impossible figures. In view of this evidence the conflicting results obtained in the case of potassium iodide on the assumption of an irregular but possible structure might conceivably be disregarded. Unfortunately, however, the evidence is by no means decisive and, as a matter of fact, only tends to emphasize the difficulty in question.

Summary

In the present paper an empirical relationship between the volume (V) of a saturated solution and the solubility (N) of the saturating salt is discussed. From this relationship there is obtained by extrapolation the limiting volume $\bar{v}$ for the hypothetical state where no water is present. The apparent volume (b) occupied by the ions in this limiting state was previously found for eight alkali salts. The space-filling quotient $b/\bar{v}$ for these eight salts is of the same order of magnitude as that of crystalline solids.

By assuming a lattice arrangement of the ions in this limiting state it is possible to calculate the radii of the individual ions. The apparent radii found in this way are, in general, larger than the corresponding radii in the crystalline state and smaller than in dilute solution. Finally, it is pointed out as a possible regularity that in the saturated state the effective volumes of the anions are the same as in dilute solutions while those of the cations are approximately the same as in the crystalline state.

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STUDIES IN PHOTOSYNTHESIS IN TROPICAL SUNLIGHT. PART I

BY G. GOPALA RAO AND N. R. DHAR

Formaldehyde Synthesis

Under the action of sunlight, the green plants absorb carbon dioxide from the air and transform it with the intervention of water into carbohydrates. This phenomenon has been technically called photosynthesis. The reaction $nCO_2 + nH_2O = (CH_2O)n + nO_2$ is endothermic and the quantity of energy absorbed is approximately 110,000 gram calories for each gram molecule of carbon dioxide. Thus in the process of photosynthesis, nature has worked out a method of utilising the enormous floods of solar energy pouring on the earth. According to Warburg, no other endothermal photochemical reaction shows such a high utilisation factor. The green plant is thus an efficient converter of the inexhaustible supply of solar energy into potential energy in the shape of food materials, fuel, etc.; coal and petroleum are likewise the product of photosynthetic activity produced ages ago. Thus it becomes evident that all life on this planet and our gigantic industrial developments of the modern era depend on this phenomenon of photosynthesis, which in the ultimate analysis is the prime mover of civilisation.

Because of its fundamental importance carbon assimilation early attracted the attention of scientific workers. Since the time of Stephen Hales (1707), this has been the subject of numerous researches by such brilliant workers as Priestley, Ingenhousz, Senebier and de Saussure. In spite of countless suggestions the mechanism of the reaction is still obscure. The theory which has held the attention for over half a century and is still the pivot of the modern investigations, is the formaldehyde hypothesis of Baeyer given out in 1864. The general consensus of opinion is in favour of the view that formaldehyde is photochemically synthesised from carbon dioxide and water, and that the formaldehyde is then polymerised to form carbohydrate. The mechanism of the formation of formaldehyde from carbon dioxide and water will be discussed in Part II.

Evidence for the substantiation of Baeyer's theory has been sought from more than one direction. These are:

(1) Attempts to find in the plant the intermediate product, formaldehyde. Evidence on this head would not be of much value as the presence of formaldehyde in the leaves is not a sure indication of its being an intermediate product, especially in view of the work of Spoehr[1] and Moore and Webster[2] who showed that many substances of vegetable origin yield formaldehyde on exposure to ultraviolet light or sunlight. However, recent experiments of Klein and Werner[3] seem to indicate that the existence of formaldehyde in

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[1] Biochem. Z., **57**, 95 (1913).

[2] Proc. Roy. Soc., **90**, 168 (1918).

[3] Biochem. Z., **169**, 361 (1926).

leaves is not due to the photolysis of certain substances existing in plants as has been suggested by the above-mentioned workers, but is really an intermediate product of assimilation.

(2) Another direction in which evidence is sought for the above theory is the feeding of plants with formaldehyde. According to Grafe[1] and Miss Baker[2] plants can utilise small amounts of formaldehyde in light, though large amounts prove toxic. Sabalitschka and Riesenberg[3] have reported that certain plants assimilate formaldehyde in the dark with the formation of sugar and starch. However, from the fact that a substance can serve as food for plants, it need not be concluded that it should be produced in the assimilation process. A more fruitful piece of evidence is furnished by the synthesis of formaldehyde "in vitro" under conditions simulating those obtaining in the plant. This phase of the problem has received new stimulus by the use of the quartz mercury vapour lamp and of fluorescent substances, which are capable of absorbing light of one wavelength and giving out light of another wavelength.

Usher and Priestley[4] obtained positive tests for formaldehyde by exposing quartz tubes containing water and carbon dioxide to ultraviolet light. Baly, Heilbron and Barker[5] claim to have obtained direct synthesis of formaldehyde from carbon dioxide. These experiments have been contradicted by Spoehr,[6] Baur and Rebman,[7] and Porter and Ramsperger.[8] Still recently Baly and coworkers[9] seem to contradict their earlier results. They say that carbohydrate and not formaldehyde is the primary product of the action of ultraviolet light on a mixture of CO_2 and water, and that the formaldehyde results from secondary photochemical action, the photolysis of the carbohydrate. On the other hand Mezzadroli and Gardano[10] have obtained formaldehyde and small quantities of sugar by exposing solutions of bicarbonates of different metals. This work is confirmed by the later experiments of Mezzadroli and Vareton[11] and Mezzadroli and Babes.[12] There is unfortunately little agreement in the results of the various workers on the reduction of carbon dioxide in ultraviolet light.

The question may well be asked of what significance for the natural process of photosynthesis are experiments on the action of ultraviolet light on carbon dioxide and water. That the ultraviolet part of the solar spectrum plays a very insignificant rôle in photosynthesis is almost certain. So at-

[1] Ber. bot. Ges., **27**, 431 (1909); **29**, 19 (1911).

[2] Ann. Bot., **27**, 411 (1913).

[3] Biochem. Z., **144**, 545 (1924).

[4] Proc. Roy. Soc., **84B**, 101 (1911).

[5] J. Chem. Soc., **119**, 1025 (1921).

[6] J. Am. Chem. Soc., **45**, 1184 (1923).

[7] Helv. Chim. Acta., **5**, 928 (1922).

[8] J. Am. Chem. Soc., **47**, 79 (1925).

[9] Proc. Roy. Soc., **116A**, 212 (1927).

[10] Atti Accad. Lincei, **6**, 160 (1927).

[11] Zymologica, **3**, 165 (1928).

[12] Gazz., **59**, 305 (1929).

tempts have not been wanting to obtain formaldehyde and carbohydrates in visible light in the presence of coloured organic and inorganic substances. Moore and Webster[1] claimed to have obtained formaldehyde by exposing solutions of colloidal uranic hydroxide through which carbon dioxide was passed. Similar results are obtained by Baly and collaborators.[2] On the other hand, entirely negative results were obtained by Baur and Rebman, and by Spoehr. Dhar and Sanyal[3] have made an extensive investigation in this line. They find the formation of formaldehyde by passing carbon dioxide through suspensions of methyl orange, methylene blue, chlorophyll, ferric chloride, uranyl salt, chromium salt etc. These experiments of Sanyal and Dhar were recently contradicted by Burk.[4]

The object of the present investigation is to see how far valid are the objections raised by Burk. As will be discussed in the following pages, some of the experimental conditions of Burk differ from those of Dhar and Sanyal and are such as would not be conducive to photosynthesis. So we are constrained to modify one or two of his experimental conditions. Otherwise the procedure is just the same, and it may be mentioned here that in most cases positive results were obtained. Thus a comparison of the present investigation with that of Burk will clearly bring into prominence the importance of experimental conditions, and shows how a change in one or more of the conditions produces altogether contrary results. The present investigation consists of:

(a) the reduction of carbon dioxide to formaldehyde in the presence of organic and inorganic photocatalysts;

(b) the reduction of carbon dioxide to carbon monoxide in the presence of light and chlorophyll.

Experimental

In nearly all the work on photosynthesis repeated previously, with a few exceptions, the experimental conditions have not been described with the detailed precision which the subject demands. In the present investigation, the experimental methods and conditions have been carefully laid down with studied care, and the points of adverse criticism have been met with.

I. *Reduction of carbon dioxide to formaldehyde.*

Carbon dioxide prepared from marble and dilute hydrochloric acid and purified by passage through two or three wash-bottles containing distilled water was passed through a two-way tube into pyrex beakers, one containing conductivity water and the other containing conductivity water to which the photosensitiser has been added. Both the beakers were covered over and exposed to the bright sun for three hours. The object of keeping a blank was to avoid the question of formaldehyde being attributed to impurities.

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[1] Proc. Roy. Soc., 87B, 163 (1913); 91B, 196 (1920).

[2] Loc. cit.

[3] J. Phys. Chem., 29, 926 (1925).

[4] J. Phys. Chem., 31, 1338 (1927).

Porter and Ramsperger (loc. cit.) in their criticism of the work of Baly and collaborators attribute the origin of formaldehyde found to the impurities present such as stopcock grease, rubber tubing, sealing wax, etc. In view of this criticism, we had to cut down the use of rubber tubing to the level of unavoidable requirements and, to prevent the action of light on rubber, it was coated over with black paper. Not content with this, we had resort to a very efficient method of proving the non-interference of impurities and it is that of putting a blank. The gas was passed through a two-way tube simultaneously into two beakers, one containing the reaction mixture and the other pure conductivity water. After three hours' exposure to bright sunlight, both the solutions were tested for formaldehyde. In every case formaldehyde was detected in the reaction mixture and never in the conductivity water kept as a blank. If any formaldehyde were to arise from stopcock grease or rubber, it should have been found in both the beakers. The entire failure to detect formaldehyde in the blank solution effectively removes the question of the impurities and clearly brings about the prominence of the photocatalysts.

The organic photocatalysts employed were: (1) methylene blue; (2) malachite green; (3) methyl orange; and (4) chlorophyll. Baur and Rebman[1] and Baur and Büchi[2] showed that formaldehyde is formed when various dyestuffs such as malachite green, eosin, rhodamine and phosphine are exposed to ultraviolet light. That aldehyde is also produced from chlorophyll and other aniline dyes in sunlight has also been shown by Osterhout.[3] In view of this work, in the experiments in which chlorophyll and other aniline dyes were used as photocatalysts we always exposed a blank solution of the dye under exactly identical conditions but no carbon dioxide was passed through it. The blank solution as well as the solution through which carbon dioxide was passed, were distilled and distillates tested for formaldehyde with Schryver's or a modified Schiff's reagent described by Déniges.[4] Comparative experiments showed that in every case in which carbon dioxide was passed considerably larger quantities of formaldehyde were produced than in the absence of carbon dioxide. These experiments repeated several times leave no doubt that carbon dioxide is reduced to formaldehyde in the presence of light and such dyestuffs.

All the tests employed for the detection of formaldehyde were first critically studied starting with dilute solutions of the substance itself. The modified Schiff's reagent was prepared as follows:

One gram of rosaniline hydrochloride was dissolved in 500 c.c. of water and to this solution 25 grms of sodium sulphite and 15 c.c. of HCl (sp. gr. 1.124) are added and the whole diluted to one litre. The solution is slowly decolorised and can be used after a few hours. In pure solution formaldehyde can be detected in a concentration of 1:500,000. Tests are carried out by adding 1 to 2 c.c. of hydrochloric acid (sp. gr. 1.124) to 10 c.c. of the solution to be tested and then 1 c.c. of the reagent. Formaldehyde produces a blue to red violet coloration. With dilute solutions, several hours are required to develop the colour, which sometimes does not attain maximum intensity until after 20 hours. Other aldehydes give only a temporary coloration.

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[1] Helv. Chim. Acta, 5, 1828 (1922).

[2] Helv. Chim. Acta, 6, 959 (1923).

[3] Am. J. Bot., 5, 511 (1918).

[4] Compt. rend., 150, 529 (1910).

The inorganic catalysts employed were colloidal ferric hydroxide, uranyl nitrate, and chromium sulphate and copper sulphate. In these cases also the solutions were distilled and distillates tested for formaldehyde. In every one of these cases formaldehyde was detected in appreciable amounts.

II. Reduction of carbon dioxide to monoxide.

The decomposition of carbon dioxide in the extreme ultraviolet light was studied by Herchefinkel[1] and later by Coehn and collaborators.[2] Berthelot and Gaudechon[3] state that the reaction

$$CO_2 \rightleftarrows CO + (O)$$

is facilitated by the presence of reducing substances. We have now shown that such a decomposition takes place in visible light from a 500-watt gas-filled tungsten filament lamp by virtue of the reducing power of methylene blue or chlorophyll.

The test employed for the detection of carbon monoxide is the well-known iodine pentoxide method of C. de La Harpe and Reverdine. Great precautions had to be taken in employing this test; for iodine pentoxide decomposes in light. So the U-tube containing iodine pentoxide was protected from all light both during and after preparation. All the joints were of glass, as iodine pentoxide is a notorious oxidising agent acting on cork, rubber and the usual lubricants. Blank experiments were always done. Traces of CO were always found in the carbon dioxide issuing out of a chlorophyll suspension exposed to light. The important bearing of this fact on the photosynthetic mechanism will be discussed in another paper.

From the experimental results recorded in Section I, ample confirmation is afforded for the work of Dhar and Sanyal, and the other workers in the field. We can now say, with a great degree of assurance that the experimental conditions of Burk were not conducive to successful photosynthesis; and hence the negative results. The distinctive feature of Burk's experimental technique was the use of condensed light. By a curious process of reasoning, Burk arrives at the conclusion that the use of lenses was found indispensable. Many of the reasons assigned are hypothetical and the arguments unconvincing. To use his own words, "the plant leaf is a veritable nest of lenses; there is no question in my mind that these natural lenses do actually increase considerably the intensity of light inside the plant." Therefore Burk used such lenses as would enable the intensity of sunlight to be increased to a maximum of five thousand fold. As against this, let us consider the common experience in photosynthesis *in vivo*, as well as *in vitro*. Falling off of photosynthesis was observed by Reinke in "Elodea" when the intensity of illumination surpassed sixty times that of sunlight and by Pantanelli when the light intensity was greater than that of sunlight. As regards experiments *in vitro*, Baly and coworkers[1] report that with increasing intensity of light (using visible light from 100-watt lamps and using coloured substances like nickel and cobalt carbonates as photosensitisers) the quantity of carbohydrate synthesised per unit quantity of light decreases. The same writers report that P. F. R. Venables, in his experiments on the quantities of organic materials, soluble in alcohol, synthesised in presence of aluminum powder and light from CO_2 and water, found that the amount synthesised decreases as the light intensity increases. In the light of such extensive and unequivocal evidence, we have no doubt in asserting that the high intensities used in Burk's experiments were harmful to photosynthesis.

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[1] Compt. rend., **149**, 395 (1909).

[2] Z. physik. Chem., **91**, 347 (1916).

[3] Compt. rend., **150**, 1690 (1910).

Summary

I. Formaldehyde has been obtained from carbon dioxide and water in the presence of the following photosensitisers and sunlight:

(1) Chlorophyll, (2) methylene blue, (3) malachite green, (4) methyl orange, (5) ferric hydroxide sol, (6) uranyl nitrate, (7) chromium sulphate and (8) copper sulphate.

Great precautions were taken in view of the adverse criticism.

II. Small quantities of carbon monoxide were obtained from the photochemical reduction of carbon dioxide by chlorophyll.

Chemical Laboratories,
University of Allahabad,
Allahabad, November 18, 1930.

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[1] Proc. Roy. Soc., **116A**, 197, 212-219, (1927).

STUDIES IN PHOTOSYNTHESIS IN TROPICAL SUNLIGHT. PART II.

BY G. GOPALA RAO AND N. R. DHAR

Photosynthesis of Formaldehyde and Carbohydrates from Alkali Bicarbonates in the Presence of Coloured Insoluble Substances

In a previous paper we have recorded our results on the photosynthesis of formaldehyde in tropical sunlight. The present paper deals with:

(1) Photosynthesis of formaldehyde and carbohydrates from alkali bicarbonates.

(2) The polymerisation of formaldehyde to reducing sugars.

(3) Discussion of results recorded in both the papers.

The exposed solutions were made up with water twice distilled, the second distillation being carried out in silica vessels; the water had a conductivity not greater than 3×10^{-6} ohm^{-1} at 30°. Merck's or Kahlbaum's chemicals were used, usually without further purification. Most of the solutions were exposed in glass bulbs blown at the end of common soft glass tubes about one and one half feet in length and 10-15 mm. in diameter. The bulbs had a capacity ranging from 50 to 150 cubic centimeters and were very transparent. The tubes were always cleaned first with hot chromic acid, then with plenty of distilled water and finally with conductivity water and dried at 100° and kept away until used. The bulbs were always sealed with a little air space above the solution. The tubes were held dipped under water in beakers and exposed to the sun for periods varying from 10 hours to 60 hours extending over several days. In tropical countries like India, the sunlight on bright days consists of light of wavelengths extending up to 2900 Å; that is, a considerable portion of the ultraviolet spectrum from 3800-2900 Å is thus represented in sunlight. But as ordinary glass transmits wavelengths only up to 3400 Å, it can safely be asserted that not much ultraviolet light takes part in our experiments.

2% solutions of Merck's sodium bicarbonate were exposed with the following catalysts:

(i) Colloidal ferric hydroxide.
(ii) Cobalt carbonate.
(iii) Nickel carbonate.

Saturated solutions of carbon dioxide in conductivity water with the above catalysts were also exposed.

After filtration, since the solutions still contain appreciable amounts of the bicarbonates of nickel and cobalt in solution, they were concentrated on a water bath. The precipitated carbonate was removed and the solutions evaporated to dryness. Part of the solution, however, was tested with Molisch carbohydrate reagent as described in Mulliken's "A Method for the Detection of Pure Organic Compounds".[1] The rest of the solution was evaporated to dryness and the residue extracted with methyl alcohol which on evaporation leaves a small residue. This residue charred on heating with concentrated sulphuric acid and did not reduce Benedict's solution until after hydrolysis with dilute hydrochloric acid at 100° and subsequent neutralisation.

In the case of colloidal ferric hydroxide, the sol was coagulated by the addition of a little potassium sulphate, filtered and the filtrate treated as above.

Sometimes, parts of the original solution were also tested for formaldehyde with Schryver's and modified Schiff's reagents. The following results were obtained:

1.	CO_2 and conductivity water sealed in glass tubes and exposed for 60 hours to sunlight.	Extremely small quantities of formaldehyde.
2.	CO_2 and conductivity water and ferric hydroxide sol exposed for 60 hours.	Small quantities of formaldehyde and carbohydrate.
3.	2% solution of sodium bicarbonate little cobalt carbonate, 45 hours' exposure.	Small quantities of formaldehyde.
4.	2% solution of sodium bicarbonate little nickel carbonate, 45 hours' exposure.	Appreciable quantities of formaldehyde and carbohydrate.

Similar tubes were kept in the dark in each case for the same length of time. On examination, the unexposed solutions yielded negative results. It may be mentioned here that results similar to the above have also been obtained by Baly and collaborators.[2]

Polymerisation of Formaldehyde to Reducing Sugars

Butlerow first observed the condensation of "dioxymethylene" (trioxymethylene) to a sugar like substance by means of alkalis. This phase of the subject has been further studied by Loew[3] and by Lobry de Bruyn and van Ekenstein[4] and lately by Nef[5] who showed that the substance so obtained is a mixture of 24 hexoses and about an equal number of pentoses. That the condensation is affected by light has been observed by various workers. Inghilleri[6] reported that by exposing sealed tubes containing formaldehyde to sunlight, he obtained 'methylenitan' a sugar like substance. Recently, Baly, Heilbron, and Barker[1] reported the formation of sugars from a solution of formaldehyde exposed to ultraviolet light. Dhar and Sanyal (loc. cit.) report the formation of reducing sugar from formaldehyde solutions exposed with little ferric chloride or methyl orange.

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[1] "A Method for the Detection of Pure Organic Compounds," **1**, 26 (1904); "Practical Organic and Biochemistry" (1915).

[2] Proc. Roy. Soc., **116A**, 212 (1927).

[3] J. prakt. Chem., **33**, 321, (1886); **34**, 51.

[4] Rec. Trav. Chim., **18**, 309 (1899).

[5] Ann., **376**, 1 (1910); **403**, 204 (1914).

[6] Z. physiol. Chem., **71**, 105 (1911).

Aqueous solutions of formaldehyde prepared by diluting Merck's pure formalin were exposed in sealed tubes to sunlight for periods extending over several hours, usually 10 to 30 hours. Similar tubes were kept in the dark in every case. The exposed and unexposed ones were examined simultaneously. As Fehling's solution is reduced by formaldehyde, it was never used in testing for reducing sugars. Benedict's solution which is reduced by sugars and not by formaldehyde was always used. The following results were obtained:

Formaldehyde + water	No reducing sugar
Formaldehyde + water ferric hydroxide sol	No reducing sugar
Formaldehyde + MgO	No reducing sugar
Formaldehyde + ZnO + water	Small quantities of reducing sugar.
Formaldehyde + methyl-orange + water.	do.
Formaldehyde + water ferric chloride	do.

In this last case the ferric chloride was photochemically reduced to ferrous salt; as it was found that ferrous salt itself reduces Benedict's solution, the ferrous salt was first removed by adding just the requisite amount of a dilute solution of potassium ferricyanide, filtering of the precipitated ferrous ferricyanide and then tested for reducing sugar.

Discussion of Results:- In Part I we have recorded evidence for the formation of formaldehyde from carbon dioxide and water exposed to tropical sunlight with small quantities of photocatalysts e.g. chlorophyll, methylene blue, malachite green or methyl orange; and inorganic substances like ferric hydroxide sol, uranyl nitrate, chromium sulphate, and copper sulphate, all coloured substances having strong absorption in the visible portion of the solar spectrum. The analogy between chlorophyll and dyestuffs like methylene blue is not far to seek. At any instant, the amounts of formaldehyde detectable is small, presumably due to the fact that the photo-synthesised formaldehyde rapidly polymerises to sugars. From an analogy with these experiments *in vitro*, it can be said with a certain amount of confidence that in the green plants too, the primary product of photosynthesis is formaldehyde, which then polymerises to sugars. The reaction therefore might be

$$CO_2 + H_2O \rightarrow HCHO + O_2$$

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[1] J. Chem. Soc., 119, 1025 (1921).

which takes place with an absorption of energy equivalent to 110,000 calories. The light energy absorbed by chlorophyll is in some mysterious way converted to chemical energy. On account of the readiness with which photo-synthesised formaldehyde polymerises to sugars, Baly and Barker differentiate it from ordinary formaldehyde by assigning a different structural formula:

$$\text{HCHO (ordinary)} \longrightarrow \text{HCOH (active)}$$

It is generally believed that chlorophyll plays the rôle of an optical sensitiser. But the mechanism of sensitisation is not yet clear. Chlorophyll in the leaves exhibits fluorescence, and is capable of sensitising photographic plates. Tswett[1] suggests that chlorophyll like all fluorescent substances undergoes a peculiar reversible change associated with intake of energy; when this reverts to the original molecular form, the energy taken up is radiated out as phosphorescent light, which is specifically absorbed by carbonic acid. On the other hand, Weigert considers that the absorption of light by chlorophyll results in an internal photoelectric effect, which finally results in the break-down of water into hydrogen peroxide and hydrogen, which then react with carbon dioxide according to the equation:

$$H_2 + CO_2 + H_2O_2 = HCHO + H_2O + O_2$$

Besides these theories, where an essentially physical function is assigned to chlorophyll, there are some which give it an active part in the chemical reactions. Of these, mention should be made of the theory of Willstätter and Stoll. They think that carbonic acid forms a complex with chlorophyll, which with absorption of energy passes into an isomeric peroxide type of compound. This breaks up thermally, probably due to the action of an enzyme, with the formation of formaldehyde, elimination of oxygen and regeneration of chlorophyll.

The experimental results recorded in the foregoing pages show that chlorophyll besides being an optical sensitiser, also acts as a reducing agent under the influence of light. It has been shown that chlorophyll photochemically reduces carbon dioxide to carbon monoxide. In the light of these results, we suggest the following mechanism for the photochemical synthesis of formaldehyde. According to this hypothesis, the photosynthesis consists of three stages:

(i) In the first stage, chlorophyll reacts with carbonic acid under the influence of light, with the formation of chlorophyll peroxide and carbon monoxide.

The change can be represented by

$$\text{Chlorophyll} + H_2CO_3 + \text{light energy} = \text{chlorophyll peroxide} + CO$$

The interaction of the nascent carbon monoxide with water to give instantaneously

$$H_2O + CO \longrightarrow HCHO + (O)$$

The occurrence of this step in the photosynthesis mechanism is also supported by the experiments of Berthelot and Gaudechon[1], who were able to obtain formaldehyde from carbon monoxide and water in presence of light. Under the action of ultraviolet light the carbon monoxide is activated and this active carbon monoxide interacts with water to give

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[1] Ber. bot. Ges., **29**, 744 (1911).

$$H_2O + CO = HCHO + (O)$$

The carbon monoxide obtained in photosynthesis, according to the present scheme, is in the active state at the moment of its formation and hence it readily reacts with water, as in the experiments of Berthelot and Gaudechon[2] This is further supported by the experiments of Bottomley and Jackson, who showed that carbon monoxide can, to a measure at least, replace carbon dioxide in photosynthesis. Here only half of the oxygen is given off.

(ii) The other half of the oxygen comes from the decomposition of the peroxide which takes place with regeneration of chlorophyll. The decomposition of peroxide is probably thermal and due to an enzyme present in the chloroplasts.

(iii) The last stage consists in the polymerisation of formaldehyde to sugars. Thus the oxygen evolution takes place in two stages. Half the amount of oxygen corresponding to the equation (final)

$$CO_2 + H_2O \rightarrow HCHO + O_2$$

is evolved when the photochemically produced carbon monoxide reacts with water giving formaldehyde and oxygen. The other half of the oxygen comes when the photochemically produced chlorophyll peroxide decomposes thermally giving oxygen and regenerating chlorophyll.

That the evolution of oxygen probably takes place in two stages is indicated by the experiments of Kostytschew[3] and confirmed by Spoehr and McGee[4] that the ratio CO_2/O_2 during illumination varies with time. Kostytschew found that during photosynthesis the leaves absorb initially a great deal more of carbon dioxide than oxygen is given off; about one third the absorbed carbon dioxide is fixed without oxygen emission. After a short time these conditions are reversed and finally CO_2/O_2 ratio attains the constant value of 1.

According to our theory of the photosynthetic process, there are two important stages. The first is the photochemical interaction of chlorophyll and carbon dioxide, giving chlorophyll peroxide and carbon monoxide. The carbon monoxide produced is very active being in the nascent condition, so it interacts with water giving formaldehyde and oxygen. The second important stage is the thermal decomposition of chlorophyll peroxide giving a further quantity of oxygen. The whole process of photosynthesis is considered to be complete when both these reactions are complete and the whole amount of oxygen is given off:

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[1] Compt. rend., **150**, 690 (1910).

[2] Proc. Roy. Soc., **72**, 130 (1903).

[3] Ber. bot. Ges., **39**, 319 (1921).

[4] Am. J. Bot., **11**, 493 (1924).

i. (a) $\text{Chlorophyll} + H_2CO_3 + \text{light energy}$
$= \text{Chlorophyll peroxide} + CO \text{ (active)}$

(b) $CO \text{ (active)} + H_2O = HCHO + (O)$

ii. $\text{Chlorophyll peroxide} = \text{Chlorophyll} + \text{water} + (O)$

Most workers have followed the kinetics of photosynthetic reaction in plants by measuring the total volume of oxygen evolved from time to time. So if the oxygen is evolved in two processes, the first reaction followed by the second, it is clear that the whole process will be limited by any one of these reactions. Suppose one of the reactions is fast, the other comparatively slow and since the whole process is measured by the total oxygen evolved in the two reactions combined, the photosynthesis will be controlled by the slower of the two reactions.

That there are two stages in photosynthesis, a photochemical and a thermal one is indicated by the work of Blackman and Miss Matthaei,[1] Warburg[2] and of Willstätter[3] on the temperature coefficient of the photosynthesis. As light is necessary for the whole process, it is clear that a photochemical reaction is involved. But photochemical reactions are characterised by low temperature coefficients; while Miss Matthaei and subsequent workers have found a temperature coefficient of 2, characteristic of thermal and enzymic reactions. That the whole process consists of two stages would explain the fact that some workers have found under certain conditions a temperature coefficient of less than 2; for if there are two stages with different temperature coefficients, the temperature coefficient of the whole process will depend upon the rate of the process which proceeds relatively more slowly—if the photochemical stage is relatively slower, the temperature coefficient of the whole process will be low; while if the purely thermal or enzymic reaction is relatively slower the temperature coefficient would be high, about 2. This different behaviour towards temperature was observed by Willstätter in the case of the green and yellow varieties of the same species,—it was found that the rate of photosynthesis of normal green leaves of "ulmas" exposed to strong light and in an atmosphere containing excess (45%) of carbon dioxide, was more influenced by temperature than that of the yellow varieties of the same species. We are of the opinion that in the yellow leaves, the chlorophyll being present in comparatively small quantities and being concerned with the photochemical reaction will determine the rate of the whole process; while in the green leaves chlorophyll will be in excess but substances participating in the thermal reaction, say enzymes, will be in relatively smaller quantity and will therefore determine the whole process. The photosynthesis in the yellow leaves being determined by the photochemical reaction, and that in the green leaves limited by the thermal reaction, it is clear that the temperature coefficient in the former case will be of the order of the temperature coefficient of a photochemical reaction, and that in the second case will be of the order of a thermal reaction; that is, the temperature coefficient in the former case will be smaller than that in the latter.

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[1] Phil. Trans., **197**, 47 (1905).

[2] Biochem. Z., **100**, 259 (1919).

[3] "Untersuchungen über die Kohlensäure Assimilation" (1918).

The experiments of Warburg on the relation between light intensity and temperature coefficient also support the hypothesis of the two stages. All conditions remaining the same, the temperature coefficient is unity when the light intensity is low and the temperature coefficient is greater than unity when the light intensity is high. In the first case, because the intensity of light is low, the photochemical reaction will be slow and hence it will limit the whole process. In the second case the intensity of light being sufficiently high the photochemical reaction will be fairly rapid; but the thermal reaction is comparatively slow. So the thermal reaction will control the whole process. Hence from the considerations already put forward, it is clear that in the former case, the process being limited by the light reaction, and in the latter by the thermal reaction, the temperature coefficient in the former case will be smaller than that in the latter case.

That an internal factor, like the content of chlorophyll with which carbon dioxide interacts, is limiting the whole process is evident from the researches of Warburg on the effect of carbon dioxide concentration on the rate of photosynthesis. With increasing carbon dioxide concentration, above a certain amount, Warburg found that the increase in the rate of photosynthesis rapidly falls off until a certain concentration of carbon dioxide; further increase in the latter produces no effect. It is clear that the rate of photosynthesis depends not only on the concentration of carbon dioxide, but on that of some other substance as well, with which carbon dioxide reacts. The experimental findings of Warburg are satisfactorily explained on the present hypothesis. According to this hypothesis, carbon dioxide interacts with chlorophyll.

Chlorophyll + carbon dioxide + water = chlorophyll peroxide + CO.

At low concentrations of carbon dioxide, when the chlorophyll is in comparatively greater quantities, it is clear that the photosynthesis will increase with increasing concentration of carbon dioxide. But this will not proceed *ad infinitum.* The content of chlorophyll being limited, a certain stage will be reached where the content of chlorophyll is no longer in excess but is just sufficient to interact with the carbon dioxide present at any instant; if the concentration of carbon dioxide is further increased, there will be no further increase in the reaction velocity, as the chlorophyll with which carbon dioxide interacts is in limited quantities. The surplus carbon dioxide finds no chlorophyll to interact with. Hence Warburg found that by increasing the concentration of carbon dioxide above a certain maximum, no further increase in the rate of photosynthesis takes place.

Influence of Chlorophyll Content

According to the present hypothesis, chlorophyll takes part in the chemical reaction and as such, the content of chlorophyll should have a profound influence on the rate of photosynthesis. Mention would be made only of the great advance made by Willstätter and Stoll in this line. The conditions under which the experiments were carried out were such that neither temperature, carbon dioxide concentration nor light intensity were determining the rate of photosynthesis. This is of course, necessary in order to emphasise or demonstrate the influence of chlorophyll content. In most of the cases, excised leaves were used. Willstätter and Stoll introduced as a measure of the ratio of chlorophyll content to the rate of photosynthesis the term "Assimilationszahl" or photosynthetic number. This is a measure of maximal synthesis expressed in grams of carbon dioxide absorbed per hour by a leaf mass containing 1 gram of chlorophyll under favourable conditions of temperature or briefly, it is the number of grams of carbon dioxide absorbed per hour per gram of chlorophyll; this is the photosynthetic number, which for the sake of brevity, we shall designate by P_c.

$$P_c = \frac{\text{hourly photosynthesis, grams } CO_2}{\text{Grams chlorophyll}}$$

$5\ \%\ CO_2$, about 48,000 lux

Species.	Temp.	Value of P_c
Aesculus hippocastanum	25°	6.4
Acer negundo	25°	7.7
Acer pseudoplatanus	25°	5.2
Ampelopsis quinquefolia	25°	6.2
Hydrangia opulodes	30°	6.5
Pelargonium zonale	30°	7.4
Sambuscus nigra	25°	6.6
Tilia cordata	25°	6.6
Ulmus	25°	6.6
Cucurbita pepo	25°	12.1
Clerodendron trichotonum Thumb	25°	12.3
Fragaria vesca	25°	10.6

In the foregoing table approximately constant values of P_c for a given temperature are obtained, the value being about 6.5. This constant value of P_c would indicate that under these conditions, the rate of photosynthesis was determined by the chlorophyll content. There is a rough parallelism between rate of photosynthesis and chlorophyll content.

In the lower part of the table are given the values of P_c for plants which have a notably rapid growth and high photosynthetic rate. In these, P_c is higher, about 12; nevertheless constant for a number of cases. The results of Willstätter and Stoll on the photosynthetic activity of leaves in different stages of development show that although the chlorophyll content of the leaves increases with age and that the photosynthetic activity also increases, the two are by no means parallel.

These results show that the photosynthetic rate depends to a large extent on the chlorophyll content.

That the thermal reaction is of the type of the decomposition of a peroxide is indicated by the work of Warburg and Uyesugé.[1]. They find that temperature, hydrocyanic acid, and urethane act in the same way on the the release of oxygen from hydrogen peroxide by "chlorella" in the dark, as on the photosynthesis in strong light.

The present theory thus accounts for most of the facts of photosynthesis in plants: firstly for the fact that the ratio of CO_2/O_2 changes; secondly for the variation of temperature coefficient with intensity; thirdly for the considerable difference in temperature coefficient of the photosynthetic reaction with yellow and green leaves of the same species; fourthly, for the observations of Warburg on the influence of carbon dioxide concentration on the rate of photosynthesis and lastly for the effect of chlorophyll content on the rate of photosynthesis.

Chemical Laboratories,
University of Allahabad,
Allahabad,
November 18, 1930.

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[1] Biochem. Z., **146**, 486 (1924).

THE COLOR CHANGES OF SULFONPHTHALEINS, BENZEINS, AND PHTHALEINS

BY I. M. KOLTHOFF

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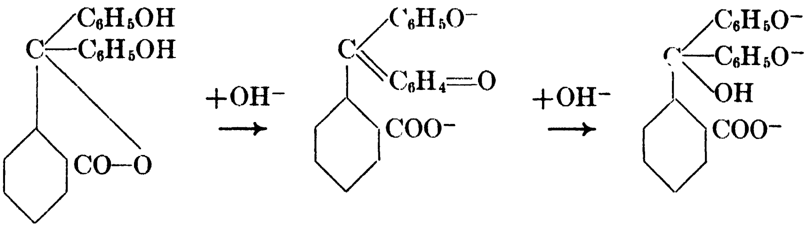
1. The Phthaleins in the Alkaline Range

Previously it has been shown,[1] that there is no conflict between the chromophoric theory and the ionization theory of the color change of an indicator. For a quantitative interpretation of the color equilibrium in an indicator solution the classical dissociation theory of Wilhelm Ostwald has to be used. The scheme given for the changes in structure and color of phenolphthalein for example:



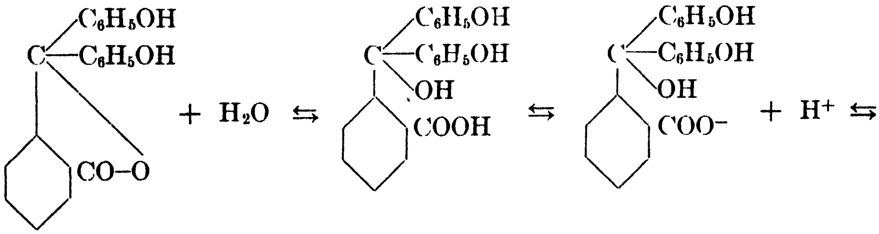
acid form; lactone; colorless

quinone-phenolate weakly alkaline form red violet

carbinolform strongly alkaline form; colorless

does not account for the influence of hydrogen or hydroxylions upon the equilibrium between the various forms. A colorless solution of phenolphthalein is mainly present in the lactone form, though the latter must be in equilibrium with other forms, the concentration of which may be extremely small.

The following scheme represents the various equilibria which have to be considered in the quantitative interpretation of the color change of phenolphthalein and similar compounds:



I Lactone Colorless

II Colorless

III Colorless

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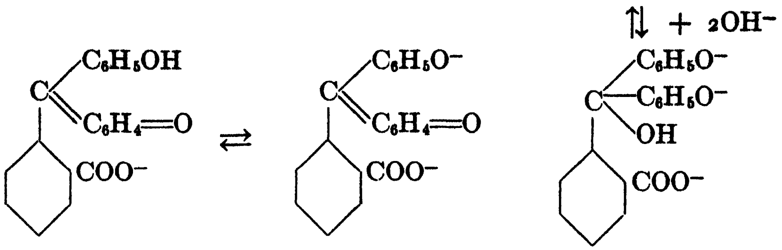
[1] I. M. Kolthoff: "Indicators," p. 239; also W. D. Bancroft and H. L. Davis: J. Phys. Chem., 34, 1797 (1930), where the literature is discussed.



IV Quinoid (probably weakly yellow)

V Quinolphenolate red violet

VI Carbinol colorless

It is known that the monovalent anions of phenolphthalein (form III) are colorless. One finds for example in the titration of an alcoholic solution of this indicator with sodium hydroxide a considerable amount of sodium hydroxide consumed before the color turns pink. According to measurements of L. Rosenstein,[2] the apparent first ionization constant of phenolphthalein is equal to 1.15×10^{-9}; the second one to 2.8×10^{-10}. Therefore:

$$\frac{[H^+]\,[III]}{[I]} = K_1 = 1.15 \times 10^{-9} \qquad (1)$$

The equilibrium between the forms I and II is reversible:

$$\frac{[I]}{[II]} = K \qquad (2)$$

or:

$$\frac{[H^+]\,[III]}{[II]\,K} = K_1 \qquad (3)$$

II represents an ordinary carboxylic acid. All these acids like benzoic acid, have an ionization constant of 10^{-5} or larger. Assuming that the ionization constant of II is also of the order of 10^{-5}, it is found from equation (3) that:

$$\frac{[H^+]\,[III]}{[II]} = 10^{-5} = K\,K_1 \qquad (4)$$

and K is of the order of 10^4.

Therefore in an aqueous solution of phenolphthalein the concentration of the lactone form is of the order of 10,000 times larger than that of the hydrated compound.[3] The concentration of the quinoid form IV (carboxylic group dissociated or undissociated) must be extremely small with respect to those of the other configurations as the solution is colorless. Addition of hydroxylions displaces the equilibrium from II to III over IV to the quinolphenolate V.

In the particular case of phenolphthalein the conditions are such that the equilibrium can quantitatively be expressed by considering the reactions:

$$I \leftrightarrows III + H^+ \qquad III \leftrightarrows V + H^+$$
$$K = 1.15 \times 10^{-9} \qquad K_2 = 2.8 \times 10^{-10}$$

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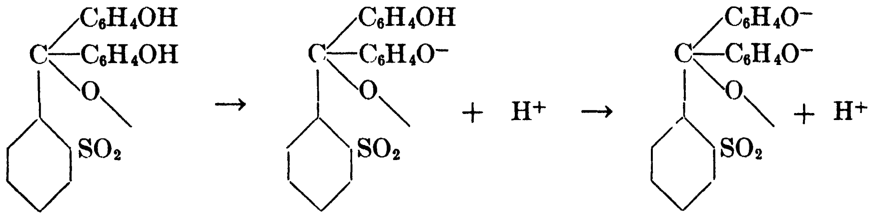
[2] L. Rosenstein: J. Am. Chem. Soc., **34**, 1117 (1912).

[3] Comp. also R. T. Birge and S. F. Acree: J. Am. Chem. Soc., **41**, 1031 (1919.)

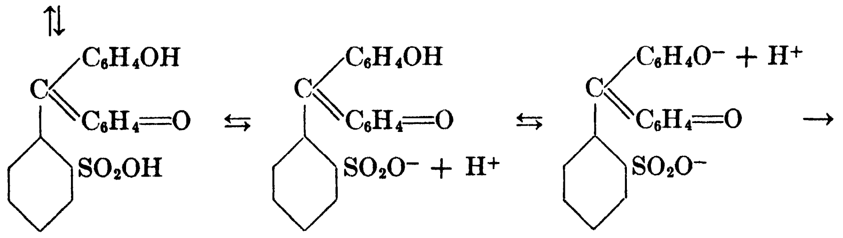
The decolorizing effect of an excess of alkali can only be explained by assuming that even in strongly alkaline medium there is some of III left, which is transformed into the colorless configuration VI (equilibrium III $\leftrightarrows$ VI. From the above it is evident that the conditions governing the color change of the phthaleins are extremely complicated. It is of interest to compare the phthaleins with the corresponding sulfonphthaleins.

2. The Sulfonphthaleins in their Alkaline Range

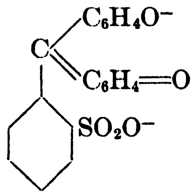
Whereas the (weakly) acid form of most phthaleins is colorless the sulfonphthaleins all are yellow in solution. The structures of all sulfonphthaleins are analogous to that of phenolsulfonphthalein (phenolred) whose various tautomers are given by H. A. Lubs and S. F. Acree[4] in the following scheme:



Ia Colorless Ib Colorless Ic Colorless



IIa slightly colored (yellow) IIb slightly colored (yellow) IIc deeply colored (quinonephenolate)



III deeply colored (?)

Even assuming that part of a sulfonphthalein in aqueous solution is present in the colorless form (compare below) it is still questionable whether it is there in the sultone form (I_a: I_b and I_c).

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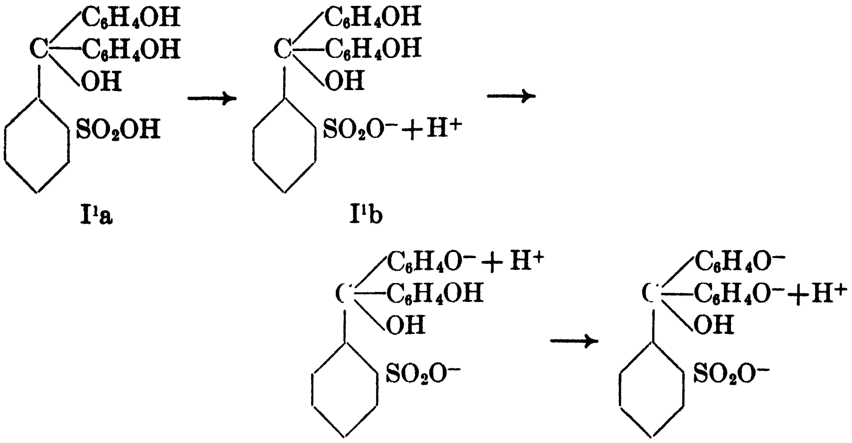
[4] H. A. Lubs and S. F. Acree: J. Am. Chem. Soc., 38, 2772 (1916); comp. also E. C. White and S. F. Acree: 39, 648 (1917) 40, 1092 (1918).

Although the sulfonphthaleins are much more stable towards an excess of alkali than the corresponding phthaleins are, they still can be partly transformed into colorless ions with carbinolstructure as Thiel[5] has shown.

These ions must be derived from the colorless configuration:



I^1_a corresponding to the hydrated form of phenolphthalein (II). Therefore instead of the scheme I_a, I_b and I_c (Lubs and Acree) the above scheme I^1_a I^1_b I^1_c I^1_d can as well be written instead. From conductance measurements White[4] has concluded, that in an aqueous solution of phenolsulfonphthalein approximately 65% of the indicator is present in the quinoid (yellow) form, and the remainder in the colorless sultone form. This however seems quite doubtful. If the above statement were true it might be expected that the intensity of the yellow color would increase upon neutralization of the strongly acid sulfonic acid group, as the equilibrium is displaced from II_a to II_b and hence from I_a to II_b. However it was found by the author that phenolred has practically the same color intensity at a pH of 3 and 5. Similarly it was observed, that the intensity of the yellow color of thymolsulfonphthalein practically did not change between a pH of 4 and 7. Therefore if any of the indicator were present in the sultone (I_a) or carbonium form (I^1_a); (the latter must be present to account for the decoloration by a large excess of alkali) their quantities must be negligibly small with respect to those of the quinoid configurations II_a and II_b. Therefore from the quantitative point of view the color change from the yellow to the alkaline form can be represented by only considering the equilibrium between II_b and II_c. Actually it has been shown that the indicator constant K_i:

$$\frac{[II_b]\,[H^+]}{[II_c]} = K_i$$

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[5] A. Thiel: Monatsheft, 53-54 1008 (1929).

is constant in the color change from yellow to the alkaline form, and that in this range there is no indication of the formation of a compound like III. The concentration of the carbinolform is so small that it need not be considered in this range of color change. It should be emphasized that the above considerations hold for aqueous solutions of the sulfonphthaleins; in other solvents the conditions may be much more complicated. The color change of the sulfonphthaleins in the alkaline range is completely comparable with that of the corresponding benzeins, where no sultone can be formed. It may be mentioned that some benzeins in strong alkali (33% potassium hydroxide) also form colorless salts, which must have a carbonium configuration.[6] The author has determined the color change interval of some benzeins.

Aurin; (Phenolbenzein) (Product of Eastman Kodak Co.) Indicator solution 0.1% in alcohol.

The color change from yellow to red takes place between pH 6.0 to 7.6; the indicator has almost the same interval as the corresponding phenolsulfonphthalein; the indicator constant of benzein is about two times larger than that of phenolred.

o. Cresolbenzein[7]; 0.1% solution in alcohol.

Color change interval from yellow to deep red between pH of 7.2-8.6.[8] This is about the same interval as found for the corresponding o cresolsulfonphthalein.

Dibromo o.cresolbenzein (Preparation Orndorff[7]).

Again the indicator has the same color change interval as the corresponding sulfonphthalein. Some difficulties were encountered with thymolbenzein and dibromothymolbenzein (both Orndorff[9] preparations.[7] 0.1% solutions of both indicators in alcohol were used.

Thymolbenzein: The indicator is extremely slightly soluble in water; at a pH of 9.0 the solution has a brownish color and shows an opalescence caused by the precipitated benzein. At a pH of 10.2 a bluish tinge is observed, the intensity of which increases at higher pH. The corresponding thymolsulfonphthalein has a color change interval between 8.0 and 9.6, and therefore is completely present in the alkaline form at a pH where thymolbenzein still shows its yellow color. From the above experiments one is not justified in concluding that the ionization constant of the phenolic group in thymolsulfonphthalein is much larger than that of the same in thymolbenzein. The difference in behavior is caused by the extremely slight solubility of thymolbenzein in water. The latter behaves like an indicator acid HI:

$$\frac{[\mathrm{I}^-]}{[\mathrm{HI}]} = \frac{K_\mathrm{I}}{[\mathrm{H}^+]} \qquad \text{and} \qquad [\mathrm{I}^-] = \frac{K_\mathrm{I}}{[\mathrm{H}^+]}[\mathrm{HI}]$$

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[6] Comp. W. R. Orndorff, R. C. Gibbs and S. A. McNulty: J. Am. Chem. Soc., **47**, 2767 (1925).

[7] Product prepared and used by the late Prof. W. R. Orndorff; obtained from the department of organic chemistry of Cornell University, Ithaca. The author expresses his sincere appreciation for this courtesy.

[8] Comp. W. R. Orndorff and S. A. McNulty: J. Am. Chem. Soc., **49**, 992 (1927).

[9] Comp. W. R. Orndorff and H. T. Lacey: J. Am. Chem. Soc., **49**, 818 (1927). Attempts to make a salt of the colorless carbinolform have failed.

If K_I is equal to H^+ the indicator is 50% transformed into the alkaline form; $[I^-] = [HI]$. However if the saturation value of HI is extremely small, then $[I^-]$ will be very small also, so that the color of the alkaline form cannot be perceived. The ratio $K_I/[H^+]$ has to decrease much more before the blue color of the alkaline form can be detected.

That the above explanation is correct could be shown by making experiments in buffer solutions containing 50% alcohol. (comp. also Orndorff and Lacey.[9]) In this medium the benzein is much more soluble than in water. By comparing thymolbenzein and thymolsulfonphthalein in the same buffer solutions it was found that the indicator constant of the former is about 2 to 2.5 times larger than that of thymolsulfonphthaleins. (instead of being about 100 times smaller as one might conclude from the experiments in aqueous medium). This could be expected; the color change of the benzein and the corresponding sulfonphthalein is governed by the same type of equilibrium; the ionized sulfonic group in thymolblue has a negatively inducing action upon the ionization of the phenolic group and therefore the indicator constants of the benzeins should be slightly larger than that of the corresponding sulfonphthaleins.

Dibromothymolbenzein: In aqueous buffer solutions:

Color at pH of 9.0 yellowish brown; at 9.2 slightly green, at 9.8 distinctly green; 10.2 bluish, at 10.6 dark blue. The corresponding dibromothymolsulfonphthalein has a color change interval between 6.0-7.6 (yellow to blue). Again the difference in behavior between both indicators is explained by the slight solubility of the benzein in water. In 50% alcohol the benzein and the sulfonbenzein show about the same behavior; the ionization constant of the former being again about two times larger than that of bromthymolblue.

It may be mentioned that the benzeins which are not too slightly soluble in water may have distinct advantages as indicators over the corresponding sulfonphthaleins. In preparing the solutions of the benzeins a strong sulfonic acid group need not to be neutralized. Moreover the color change takes place from the neutral form to the monovalent anion, and it can be expected that the "salt error" of the benzeins will be much smaller than that of the corresponding sulfonphthaleins.

A few words should be said of the derivatives of α Naphtol. α Naphtolphthalein is an indicator, used by S. P. L. Sörensen[10] in his pioneer work. The alcoholic and aqueous solutions of the indicator are not colorless as those of most other phthaleins are, but have a brownish color. α Naphtolphthalein changes its color in aqueous buffer-solutions between pH 7.8 to 8.8 (bluish green). The corresponding α naphtolsulfonphthalein has a color change interval between pH 7.5-9.0 from yellow to blue. α Naphtolbenzein (Eastman Kodak Co. product) again is very slightly soluble in water. In aqueous buffer solutions it changes its color between pH 10.0-11.6 (approximately) from yellow to greenish blue. In buffer mixtures made up in 50% alcohol however it shows the same behavior as α naphtolphthalein. α Naphtolsulfonphthalein and α naphtolbenzein have an indicator constant of about the same magnitude. From this and the yellow-brown color of α naphtolphthalein in acid medium it may be concluded, that in aqueous solution the latter indicator is mainly present in the quinoid form (comparable with form II_a of the sulfonphthaleins, but write in the scheme instead of the phenolgroups 2 α naphtol groups and instead of the sulfonic group the carboxylic group). The above view is supported by another fact, namely that α naphtolphthalein in its color change behaves like a monobasic acid. In this respect it is also of interest to mention, that A. Thiel[5] found the colored alkaline form quite stable in strongly alkaline solution; a behavior quite different from that of other simple phthaleins but more comparable to that of sulfonphthaleins. For the organic chemist it is an interesting problem to find out why the structure of α naphtolphthalein is different from that of phenolphthalein, o cresolphthalein, thymolphthalein etc.; or better why in solutions of the former the equilibrium between the various forms is shifted so much to that of the quinoid configuration.

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[10] S. P. L. Sörensen: Compt. rend., Lab. Carlsberg 8, 1 (1909).

3. The Sulfonphthaleins in their Strongly Acid Range

In their classical paper Clark and Lubs (1916) already stated that thymolsulfonphthalein has two ranges of color changes, one between pH 1.2 to 2.8 (red to yellow) and the other from 8.0 to 9.6 (yellow to blue). B. Cohen observed that m. cresolsulfonphthalein shows a similar behavior (acid range 0.5 to 2.5; alkaline range 7.6-9.2). This color change in strong acid medium is not restricted to thymolblue and m. cresolpurple but all sulfonphthaleins show a color change in strong acid medium. In monographs on indicators no interpretation of the structural change accounting for this color virage is given, nor is it stated to which group this effect is to be attributed. These points will be further discussed below.

In the following table the colors of various sulfonphthaleins is given at different concentrations of hydrochloric acid and in concentrated sulfuric acid.

The color changes of phenolsulfonphthalein and its dichloroproduct (C.P.R.) in strongly acid medium are not very pronounced. The colors reported (orange) have been observed in transmitted light; the reflected light being nicely pink. From the table it may be inferred that all sulfonphthaleins have two ranges in acidity at which they change their colors. Again it is of interest to compare the behavior of the benzeins to that of the corresponding sulfonphthaleins.

It has been mentioned in §2 that thymolbenzein and its dibromo derivative are extremely slightly soluble in water. In aqueous medium the color changes of these benzeins is observed at a much higher acidity than those of the corresponding sulfonphthaleins. In a medium of 50% alcohol they approach those of the sulfonphthaleins, though the change still takes place at a higher acidity. Phenolbenzein does not show a distinct color change in strongly acid medium; it has been mentioned already that the colors of the strongly acid forms of phenolsulfonphthalein and chlorphenol red are not very pronounced either. o. Cresolbenzein and its dibromo derivative show the same behavior as the corresponding sulfonphthalein.

TABLE I

Color of Sulfonphthaleins in Strongly Acid Medium

Concentration HCl	T.B.;	P.R.;	C.P.;	C.R.;	B.T.B.;	C.P.R.;	B.P.B.;	T.B.P.B.;	B.C.P.;	B.C.G.
0.001 N	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
0.01 "	orange-red	brownish-yellow	orange	orange	"	"	"	"	"	"
0.1 "	red-*violet*	*orange*	red-*pink*	orange-*pink*	"	"	"	"	"	"
1 "	"	"	"	red-pink	"	"	"	"	"	
4 "	"	"	"	"	orange-red	orange	"	"	orange	orange
6 "	"	"	"	"	*violet*	red-*orange*	"	"	orange-red	"
12 "	"	"	"	"	"	"	orange-pink	weakly yellow	*violet-red*	*violet*
H_2SO_4	"	"	"	"	purple	"	violet-red	weakly violet	"	intensely violet

T.B. = thymolsulfonphthalein;
C.P. = m. cresolsulfonphthalein;
B.T.B. = dibromothymolsulfonphthalein;
B.P.B. = Tetrabromophenolsulfonphthalein;
B.C.P. = dibromocresolsulfonphthalein;
P.R. = Phenolsulfonphthalein;
C.R. = o cresolsulfonphthalein;
C.P.R. = dichlorophenolsulfonphthalein;
T.B.P.B. = Tetrabromophenoltetrabromosulfonphthalein;
B.C.G. = Tetrabromo o. cresolsulfonphthalein;

TABLE II

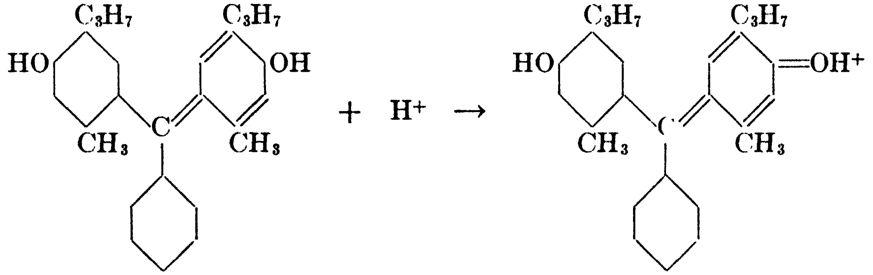
Color Change of Benzeins in Strongly Acid Medium

Concentration HCl	T.Bz.	P.Bz.	o C.Bz.	B.T.Bz.	B.C.Bz.
0.01 N	yellowish	yellow	yellow	yellow	yellow
0.1 "	pink	"	orange-pink	"	"
1 "	pink-red	"	*pink*	"	"
4 "	"	"	"	"	orange
6 "	" "	"	"	orange	*pink*
12 "	"	"	"	*red*	red
H_2SO_4	"	"	"	violet	violet-red

T.Bz. = Thymolbenzein;
P.Bz. = Phenolbenzein (Aurin);
o.C.Bz. = o.cresolbenzein;
B.T.Bz. = Dibromothymolbenzein;
B.C.Bz. = Dibromo o.cresolbenzein.

It is known that the benzeins have a weakly basic character. A. von Bayer[11] prepared the sulfate of benzaurin in the solid state; W R Orndorff and H. T. Lacey[9] obtained the sulfate, chloride and perchlorate of thymolbenzein.

Therefore it is evident that the color change of the benzeins is governed by the basic character of the quinoid group:



yellow Thymolbenzein red

It is not easy to decide whether this strongly acid form (red) is an oxonium (as given above) or carbonium compound. On the basis of the work carried out by M. Gomberg and Cone,[12] one would be inclined to favor the quinocarbonium configuration.

It is peculiar that the ionization of the quinone group has such an enormous influence upon the absorption spectrum of the compound. The free quinone has a yellow color, its cation is red to red-violet, whereas (in alkaline medium) the quinonephenolate has an intense blue color. The maximum in the absorption band shifts with this color change to higher wave lengths. From the studies made by W. R. Orndorff and collaborators[13] it may be concluded that a similar shift to longer wave lengths takes place when the yellow form is transformed into the strongly acid configuration, although the maximum is found at a shorter wave length than in alkaline medium.

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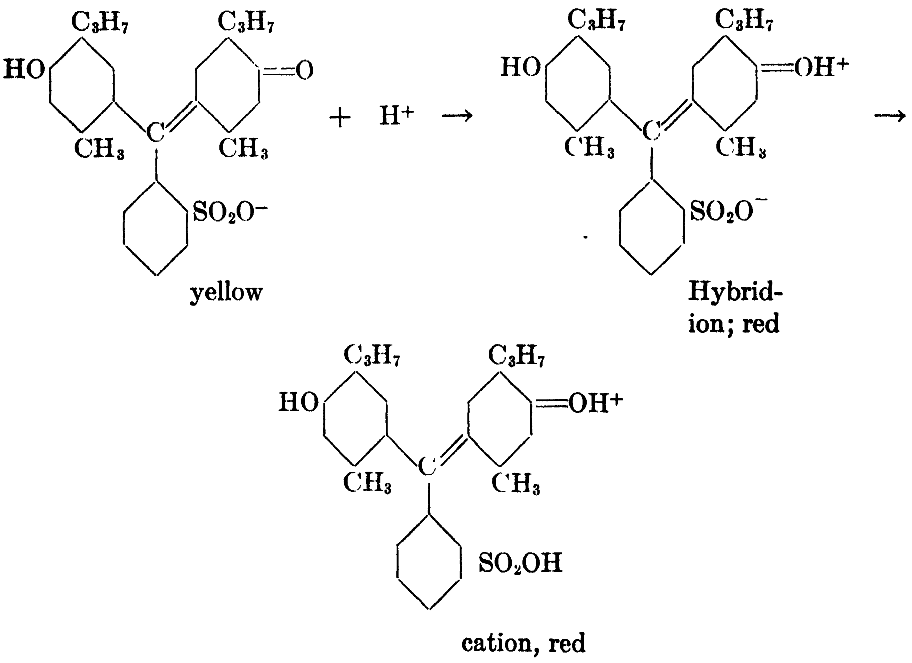
[11] A. von Bayer and R. Hallensleben: Ber., **36**, 2791 (1903).

[12] Gomberg and Cone: Ann., **370**, 192 (1909); comp. also H. Lund: J. Am. Chem. Soc., **49**, 1346 (1927); L. C. Anderson and M. Gomberg: **50**, 203 (1928); Anderson: **51**, 1889 (1929); **52**, 4567 (1930).

Moreover in these studies it is shown that the absorption coefficient of the alkaline form is greater than that of the acid form (alkaline color more intense than that of acid form).

From the analogous behavior of the benzeins and the sulfonphthaleins it may be concluded, that the color change of the latter in strongly acid medium is also caused by the ionization of the quinoid group:

Therefore it can be represented by the following scheme: (thymolsulfonphthalein).



There are various reasons for assuming that in the color change of thymolsulfonphthalein in the acid range the red hybrid ion is formed, though in stronger acid medium part of the sulfonic group will be present in the undissociated state.[14] However the colors of the hybrid ion and cation will be the same.

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[13] W. R. Orndorff and S. A. McNulty: J. Am. Chem. Soc., 49, 992, 1588 (1927); Orndorff, Gibbs and McNulty: 47, 2767 (1925) Orndorff, Gibbs, McNulty and Shapiro: 49, 1545 (1927).

[14] Comp. the analogous behavior of dimethylaminoazobenzene sulfonic acid (methyl-orange acid); I. M. Kolthoff: Rec. Trav. chim., 44, 68 (1925).

The salt error of thymolblue in its acid range is very small;[15] the solubility in aqueous medium reaches a minimum at a hydrochloric acid concentration of about 0.1 N.

The solubility of thymolsulfonphthalein was determined in water and in solutions of hydrochloric acid of various strengths (at 25° ± 1°). The solubility seems to depend relatively much upon the size of the fine powder present as a solid body. If a solution of thymolblue was precipitated by hydrochloric acid a much higher solubility was found than if the solution of the same acid normality was saturated by shaking it with solid thymolblue. The supersaturated solutions are stable for a long time; it takes more than a month before equilibrium is attained. In the experiments described below a sample of thymolsulfonphthalein obtained from Hynson, Westcott and Dunning, Baltimore, Md. was used.[16]

The product was shaken with water, and finally washed a long time with conductivity water. Part of the finer particles went into colloidal solution. Though the solubility of thymolblue is very small, it still took 30 to 90 hours shaking before the solutions were saturated. The solid particles are difficultly wetted by water. The saturated solutions were filtered and the solubility determined colorimetrically in 2-3 N hydrochloric acid. Comparison was made with solutions of thymolblue of known concentration at the same acidity.

TABLE III

Solubility of Thymolsulfonphthalein in Water and Hydrochloric Acid

Solvent	Mg. thymolblue per liter	Molarity of saturated solution
Water	110	2.3×10^{-4}
0.01 N HCl	7 2	1.55×10^{-5}
0.05 ” ”	2.6	5.6×10^{-6}
0.1 ” ”	1.8	4×10^{-6}
0.2 ” ”	1.8	4×10^{-6}
0.5 ” ”	1.6	3.5×10^{-6}
1 ” ”	1.8	4×10^{-6}
6 ” ”	5.0	1.1×10^{-5}
0.1 N HCl + 0.9 N KCl	0.8	1.8×10^{-6}

The solubility reaches a minimum in about 0.1 N hydrochloric acid. In 0.5 N acid a slightly smaller solubility is found, but probably this is due to the salting out effect of the electrolyte. In 0.1 N acid and 0.9 N, potassium chloride a solubility about half of that in 0.1 N hydrochloric acid was found. At higher acidities than 0.5 N the solubility increases slightly with the acid concentration, probably on account of the formation of the undissociated sulfonic acid group (cation).

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[15] Comp. I. M. Kolthoff: J. Phys. Chem., **32**, 1820 (1928); **34**, 1466 (1930).

[16] The author expresses his sincere appreciation to this concern for its kindness in furnishing him with a sample of their purest product. According to the conductimetric titration with sodium hydroxide it was 98 to 99% pure.

The solubility of thymolblue in water corresponds to 2.3×10^{-4} molar. Assuming that the red hybrid ion dissociates completely into hydrogen ions and the yellow anions, we have: $[H^+] [I^-] = (2.3 \times 10^{-4})^2 = 5.3 \times 10^{-8} =$ solubility product of the hybrid ion.

From the indicator function in acid medium (comp. Kolthoff[15] 1930) we know that the indicator constant

$$\frac{[H^+] [I^-]}{[{}^+I^-]} = 2.2 \times 10^{-2}$$

$[I^-]$ represents the concentration of the yellow form; $[{}^+I^-]$ the same of the red hybrid ion. From these two equations it is found, that a solution saturated with the hybrid ion contains $\frac{5.3 \times 10^{-8}}{2.2 \times 10^{-2}}$ = approximately 2×10^{-6} moles of the latter per liter. This figure is of the order of the solubility which was found in 0.1 N hydrochloric acid.

That the sulfonphthaleins in strongly acid medium behave like cations could be shown by their behavior as adsorption-indicators.[17]

From the studies of Fajans and collaborators it is known, that a silver halide negatively charged by an excess of halide ions has a tendency to adsorb cations. If these adsorbed ions are colored they usually impart to the precipitate a characteristic color. The following experiments have been made with silver thiocyanate freshly precipitated from the solution containing the dyestuff. In presence of an excess of silver ions the precipitate is positively charged, with an excess of thiocyanate ions it has a negative charge.

Methylred in neutral solution (yellow):

With an excess of silver ions red precipitate; change to yellow with an excess of thiocyanate. The positively charged precipitate adsorbs the (yellow) anions of methylred and forms a red compound at the surface.

Methylred in about 1 N sulfuric acid (red):

With an excess of thiocyanate the precipitate is brick red, and almost colorless, when positively charged. Therefore in acid medium we find the reverse behavior from that in neutral solution, owing to the fact that methylred in strongly acid medium is present in the cation form.

Methylorange shows a behavior exactly analogous to that of methylred. At its isoelectric point the presence of anions of methylorange can also be detected by its behavior as adsorption-indicator.

Tropeolin OO behaves like methylorange; in acid medium the negatively charged silver thiocyanate assumes a blue color by the adsorption of the indicator. In a similar way the cations in a red solution of pentamethoxytriphenylcarbinol can be detected if silver-iodide is used as an adsorbent.

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[17] The following experiments are not important from analytical point of view. The adsorption indicators described in the literature for argentometric titrations are preferable to those mentioned in this paper.

Thymolsulfonphthalein in about 1 N sulfuric acid is only slightly adsorbed by positively charged silver thiocyanate, with an excess of thiocyanate ions the precipitate turns deep violet, indicating the cation function of the indicator.

In neutral solution (yellow) thymolblue does not color the precipitate, neither with an excess of silver nor with thiocyanate.

Phenolsulfonphthalein shows qualitatively a similar behavior. In 1 N sulfuric acid the precipitate has a pink color with an excess of thiocyanate, and it is decolorized by an excess of silver ions.

From the above it is evident that the color change of the sulfonphthaleins in strongly acid medium has to be attributed to a cation formation of the basic quinone group. From the experiments listed in Table 1 and other observations the following conclusions could be drawn:

1. The basic character of the quinone group decreases with the introduction of halogens in the phenolic group:

K_{Base} Phenolred > K_{Base} Chlorophenolred > K_{Base} Bromophenolblue > K_{Base} Tetrabromphenolblue..

2. The maximum absorption of light by the quinone cation shifts to longer wave lengths with the introduction of halogens (for example in strongly acid medium: phenolred is orange; dichlorphenolred red orange; tetrabromphenolsulfonphthalein violet red (H_2SO_4). Qualitatively therefore the introduction of halogens has a similar influence upon the absorption of light by the alkaline form as it has upon the strongly acid configuration.

3. The same similarity holds when light absorptions by the alkaline and strongly acid forms of phenol, thymol, cresolsulfonphthaleins are compared.

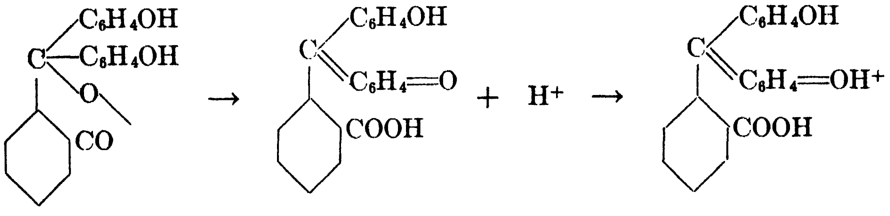
Many of the sulfonphthaleins in the solid form are strongly colored dark crystals or powders, like thymolblue, phenolred etc.[18]

Orndoff attributes this color to an inner salt between the quinone and sulfonic group (not ionized). There seems more reason to consider these strongly colored compounds as hybrid ions. In agreement with this view is the fact which Orndoff and Cornwell[8] found that thymolsulfonphthalein forms an ammonium salt with dry ammonia, but it does not give a salt with hydrochloric acid. Ammonia liberates the extremely weak basic quinoid group in the undissociated state, whereas dry hydrochloric acid is not able to replace the sulfonic acid ion. In own experiments it was observed that the darkly colored solids are difficultly wetted by water, which fact also seems to be in harmony with the hybrid ion view.

[18] Comp. the interesting and important studies of W. R. Orndorff and collaborators (lit. ref. 8, 9, and 13) also: W. R. Orndorff and F. W. Sherwood: J. Am. Chem. Soc., **45**, 486, 495 (1923); **48**, 2212 (1926); Orndorff and A. C. Purdy: **48**, 2212 (1926); Orndorff and C. Wang: **47**, 290 (1925); **49**, 1284 (1927); Orndorff and R. T. K. Cornwell: **48**, 981 (1926); Orndorff and I. T. Beach: **50**, 1416; Orndorff and C. V. Shapiro: 1730 (1928); Orndorff and M. L. Willard: **51**, 1466 (1929), R. T. K. Cornwell and A. J. Esselstyn: **49**, 826 (1927).

4. The Color Changes of the Phthaleins in Strongly Acid Medium

It has been known for a long time that phenolphthalein has a pink color in extremely strong acid solution. Other phthaleins show a similar behavior. Attributing this color change again to the basic character of the quinone group it may be expected that the change takes place at much higher acidities than at which the corresponding sulfonphthaleins or benzeins change their colors.



Lactone

Quinoid

Strongly acid form;
colored

In §1 it has been shown that phenolphthalein and thymolphthalein are practically completely present in the lactone form, and therefore we may expect a similar difference between the "apparent" basic strengths of thymolphthalein and thymolbenzein in strongly acid medium as there is between the "apparent" acid strengths of the thymolgroup in both indicators in their color change at the alkaline range. So it was found that thymolphthalein is still colorless in 6N hydrochloric acid; it is weakly pink in 9 N hydrochloric acid; and dark violet in concentrated hydrochloric acid and sulfuric acid. Thymolbenzein is completely transformed into the acid form in 1 N hydrochloric acid. Phenolphthalein shows a weakly pink color in 9 N and 12 N hydrochloric acid and assumes a brown orange color in sulfuric acid. In reflected light a pink color is observed, similar to that of phenolsulfonphthalein in the same medium (see 3).

α Naphtolphthalein again behaves like α naphtolbenzein. Both indicators are colorless in 6 N hydrochloric acid, slightly green in 9 N acid, darker green in concentrated hydrochloric and sulfuric acid. On standing a green precipitate settles out. This similar behavior again is a proof that α naphtolphthalein in solution has a quinoid structure.

Summary

1. In an aqueous solution of phenolphthalein the concentration of the lactone form is of the order of 10,000 times larger than that of the carboxylic acid configuration.

2. The color change of the sulfonphthaleins in their alkaline range is quantitatively governed by the equilibrium between the quinone and the quinone phenolate (anion) forms.

3. Benzeins which are not too slightly soluble in water have advantages over the corresponding sulfonphthaleins as indicators.

4. α Naphtholphthalein in aqueous solution is mainly present in the quinoid form.

5. The color change of sulfonphthaleins, benzeins and phthaleins in acid medium is to be attributed to the weakly basic character of the quinone group. Thymolblue forms a hybrid ion in its color change in the acid range.

6. By examining the behavior of dyestuffs as adsorption indicators it is possible to decide whether they are present in the form of cations or of anions.

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University of Minnesota,
Minneapolis,
November, 1930.

THE ACTION OF IMMISCIBLE ORGANIC LIQUIDS ON COLLOIDAL GOLD

BY T. R. BOLAM AND J. CROWE

Introduction

The most important paper concerning the behaviour of gold hydrosols when shaken with immiscible organic liquids is one published by Zsigmondy[1] in 1916. In the first place Zsigmondy examined the effect of purifying the liquids, which had apparently not been done by Reinders,[2] the first to study the subject at all extensively. It was found that pure benzene, toluene, ether, carbon disulphide and amyl alcohol had no action upon the alkaline sols obtained by the Zsigmondy methods of preparation. Further, that pure benzene, toluene, and ether produced no change in the acid sols prepared by Donau's method (reduction of gold chloride by carbon monoxide) or in Zsigmondy sols acidified by the addition of hydrochloric acid, provided the concentration of hydrogen ion did not exceed about 10^{-3} grm. ion litre. On the other hand if the sols were shaken with an impure liquid, e.g. ether which had stood in the laboratory for a prolonged period, all the gold collected in the form of a blue film at the liquid-liquid interface, as had been observed by Reinders.

Zsigmondy discovered that the presence of exceedingly small quantities of protein also caused the gold in the acid sols to be shaken out by the organic liquid. In searching to explain this and the fact that excessive acidity led to the same result, experiments were carried out on suspensions of coarse gold, prepared by coagulating sols by ultrafiltration, evaporation, or the addition of electrolyte. Whether the coagulum was washed free from electrolyte prior to suspension or not, the gold particles always accumulated at the junction of the two liquids. Finally a grey-violet sol was prepared by the electrical disintegration of gold wire (Bredig's method) in pure water contained in a quartz vessel, and shaken with purified benzene. It was found that the colloidal gold was unaffected, whereas the coarser material again adhered to the organic layer.

Zsigmondy concluded that the tendency of gold particles to go to the boundary between the aqueous and organic phases was primarily a function of the degree of dispersion of the gold. He suggested that attractive forces existed between the droplets of emulsified organic liquid and the gold particles, which increased as the latter became larger. Wiegner's[3] observation that coarse ultramicrons appear to act as coagulation centres in unstable sols could be interpreted in a similar fashion. Zsigmondy thus considered that the primary particles of a gold sol were unaffected by shaking with a pure organic liquid and that the effect of added substances was due to the coagulation of the sol to form the coarser secondary complexes. To quote from his paper "Die in Wasser gelösten Verunreinigungen (bei sauren Goldlösungen

z. B. Eiweisssubstanzen) bewirken zünachst Koagulation des Goldes, dass dann in Form gröberer Teilchen stets an die Grenzfläche geht, daselbst ein metallschimmerndes Häutchen bildend. . . ."

With regard to other possible factors Zsigmondy was not very definite. He points out that the presence of (a) negative electrical charges and (b) water sheaths (Wasserhüllen) at the surfaces of the gold particles and of the benzene droplets will oppose the tendency of these bodies to unite. He also says "—die in der organischen Flüssigkeit (Aether, Benzol, Amylalkohol—) enthaltenen Verunreinigungen können, falls sie an der Oberfläche sich anreichern, wie flüchtige Fettsaüren u.dgl, auch direkte Vereinigung der Flüssigkeitströpfchen mit dem Gold und damit Koagulation veranlassen."

Freundlich[4] has remarked that it is difficult to account for the absence of effect in the case of the small colloidal particles, since these were not necessarily in a more highly charged condition than the larger ones, for the difference was shown by particles belonging to the same system (Zsigmondy's experiment with the Bredig sol.)* Viewing the problem as essentially a question of preferential wetting, he suggests that the interfacial tension between gold and water decreases as the particle becomes smaller, which makes it more difficult for the organic liquid to displace the water from the gold surface. In other words, the water sheath is more firmly bound, the smaller the particle.

The present authors commenced an investigation with the object of determining the "critical" size which, according to the views outlined above, a particle must possess if it is to be removed from the aqueous phase to the liquid-liquid interface. Preliminary experiments, however, indicated that in certain systems at least, the influence of particle size is of minor importance. The following is an account of a study of these systems.

Preliminary Experiments

Nordenson[5] has shown that the reduction of gold chloride by hydrogen peroxide is accelerated by ultraviolet light, the size of the particles in the resulting sol or suspension decreasing as the exposure is made longer. Advantage was taken of this circumstance to prepare a series of sols of different degrees of dispersion. On examining the behaviour of these systems when shaken with purified amyl alcohol (see below) it was found that in every case the whole of the gold collected immediately at the water-alcohol interface. This result was surprising since, judging from their appearance, the finer grained sols were quite comparable, in regard to particle size, with those studied by Zsigmondy. It was noticed however that Zsigmondy (see Introduction) had not observed the action of *amyl alcohol* on *acid* sols, with which we are here concerned. The possibility of the existence of specific differences between organic liquids was thus indicated and it was decided to investigate the action of a considerable number of organic liquids on both Nordenson and Zsigmondy sols.

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* See however, Freundlich and Loebmann.[11]

Examination of a Variety of Organic Liquids

Preparation of the Sols.—The Nordenson sol (Au_NA) was prepared as follows. Two c.c. of 0.6 percent Merck's gold chloride ($HAuCl_4.4H_2O$) and 0.6 c.c. of 0.1 M anhydrous potassium carbonate (Kahlbaum) were mixed with 120 c.c. conductivity water in a large porcelain basin, 0.4 c.c. of "perhydrol" (Merck) added, and the contents of the basin immediately subjected to direct radiation from a mercury vapour lamp. The exposure lasted for 25 sec. and the reduction mixture was constantly stirred during the reduction. It was found that the addition of potassium carbonate, though in quantities insufficient to produce a neutral or alkaline sol, ensured a high degree of dispersion. (cf. Beaver and Muller[6]). To prepare the Zsigmondy sol (Au_2A), 2.0 c.c. of the same gold chloride solution were diluted with 120 c.c. conductivity water, heated in a Jena glass beaker and 3.0 c.c. of 0.1 M potassium carbonate (as above) added. When the solution was just boiling the flame was removed and 3.0 c.c. of 0.4 percent pure formaldehyde (prepared in this laboratory by Dr. Coutie) added drop by drop with vigorous stirring. Water of spec. cond. $= 0.4 - 0.8 \times 10^{-6}$ mhos, prepared in a Bourdillon still, was used in the preparation of the sols and the solutions were made up with distilled water of particularly good quality (spec. cond. $= 1 - 2 \times 10^{-6}$ mhos.).

It will be noted that the concentration of the gold was the same in the two sols. Both preparations were of a deep cherry red colour and neither showed a trace of opalescence. They were stored in well-cleaned Jena glass-stoppered bottles and proved to be very stable.

Distribution Experiments.—Three c.c. of sol and 1 c.c. of organic liquid were pipetted into a tube closed with a glass stopper and the mixture shaken vigorously by hand. The tube was given 400 shakes except when all the gold was removed from the aqueous phase by less shaking.*

In order to obtain reproducible results it was found necessary to clean the tubes and stoppers very thoroughly. After washing with hot water and rectified spirits, they were immersed in aqua regia to dissolve any gold left from a previous experiment, and then placed in chromic acid overnight. Finally they were well washed with distilled water and dried in an air oven. When first used the tubes were subjected to a prolonged steaming-out. The use of tubes closed with corks was found to be unsatisfactory, at least in the case of alcohols. Apparently the irregularities observed could be traced to material dissolved from some of the corks by the organic liquid. While reproducible results were obtained by selecting new corks which presented an unbroken surface to the contents of the tube, it was considered advisable to get glass-stoppered tubes made for the investigation.

The majority of the organic liquids as obtained were either commercially pure or else had been purified in the department for research work. Finally the following were found to have absolutely no action upon either type of sol: *benzaldehyde, benzene, bromo-benzene, carbon disulphide, carbon tetrachloride, chloroform, o.m.* and *p.chlorotoluene, ether, ethyl benzene, paraffin, salicylalde-*

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*This rule was adopted throughout the work.

hyde, *toluene* and *m.xylene*. In some instances fractional distillation was necessary in order to obtain a negative result. To avoid contamination of the liquids a distillation apparatus with ground-glass joints was constructed. It was provided with a column of Raschig rings and an Anschütz thermometer was suspended above the column by means of platinum wire.

Even after distillation the toluene and xylene still possessed a slight but quite definite influence upon Au_NA, which however was eliminated by the following methods of purification. The toluene was boiled with aluminium chloride and the black product distilled, the distillate washed with sodium bicarbonate and water and allowed to stand overnight in contact with sodium wire. The organic liquid was now shaken with twelve changes of pure concentrated sulphuric acid, then repeatedly washed with distilled water, and after drying over sodium wire, fractionally distilled. The xylene was shaken with an equal volume of concentrated sulphuric acid and then treated with saturated sodium chloride. After several hours the crystals of sodium xylene sulphonate were filtered off, dried, and boiled with absolute alcohol, the sodium chloride removed by filtration, and the solution evaporated to dryness. The xylene was recovered by steam distillation with superheated steam, separated from the water in the distillate, dried with anhydrous potassium carbonate, and fractionally distilled.

Several immiscible alcohols were now examined. A. R. *amyl alcohol*, "nitrogen and pyridine free", (by B.D.H.) was shaken with four lots of caustic soda solution, well washed with distilled water and dried with anhydrous potassium carbonate. The bulk distilled over between 130.8° and 131° (B.P. iso-amyl alcohol = 131°) and this was used in the experiments. While Au_ZA was not affected in the slightest by this organic liquid (after 400 shakes) Au_NA underwent immediate change, the whole of the gold accumulating to form a blue film at the water-alcohol interface in about 5 shakes. Exactly the same results were obtained with *n-butyl*, *iso-butyl*, *hexyl* and *heptyl alcohols*. In these instances A.R. materials (by B.D.H.) were distilled and the fraction boiling over a range of 0.2°C. at the correct boiling point employed.

The Action of the Alcohols

Experiments were now carried out to ascertain the cause of the difference in behaviour of Au_ZA and Au_NA when shaken with an immiscible alcohol. As indicated above the two sols were identical in appearance. They moreover were seen to closely resemble one another when examined in the slit ultramicroscope: in both cases the majority of the particles were green, there being only a small proportion of red or orange ones.* The only obvious difference between the sols was that Au_ZA contained a larger amount of potassium carbonate than Au_NA. Hence the effect of adding this salt to a Nordenson sol was next studied.

For the reason given later a sol, Au_NB, prepared with 0.8 c.c., 0.2 N K_2CO_3 instead of 0.6 c.c. was used. A series of tubes were set up, each tube containing

*See later for determination of particle sizes.

a mixture of 3 c.c. Au_NB + 1 c.c. K_2CO_3 (Kahlbaum), the concentration of the latter increasing from tube to tube. After standing for 24 hours, the mixtures were carefully examined for any colour change, and then each was shaken with 1 c.c. amyl alcohol. As far as the action of potassium carbonate alone was concerned, no change could be detected in the sol, provided the final concentration (C) of the *added* carbonate did not exceed about 30 m.equivalents/liter. As will be seen from the following summary, within limits potassium carbonate prevented the shaking out of the sol. The values of C are approximate.

C	0.0	0.0-0.5	0.5-3.0	3.0-12.5	12.5 & over
Film formation	complete	decreasing	none	increasing	complete

That portion of the gold which did not go to the interface in any given case appeared to be quite unaffected.

It will be noted that at the higher concentrations of carbonate the sol became unstable again. To complete the comparison, the effect of adding potassium carbonate to a Zsigmondy sol was investigated. The following results were obtained with a sol, Au_ZB,* prepared with 1.5 c.c. 0.1 M,K_2CO_3 instead of 3.0 c.c.

C	0.0-5.0	5.0-15.0	15.0 & over.
Film formation	None	increasing	complete.

The concentration of carbonate required to produce the first sign of coagulation in 24 hours (i.e. in the absence of the alcohol) was about 35×10^{-3}M, which, as in the case of Au_NB, was well above the value at which film formation commenced.

Formation of Red Films.—Since the stabilising action of potassium carbonate might well be due to its alkalinity, the influence of sodium hydroxide (solution prepared from "pure" sticks) on Au_NB and Au_ZB was investigated in exactly the same fashion as above. Table I contains the results for typical series.

The occurrence of *red* films, which does not appear to have been observed by previous workers, is of particular interest since it shows that coagulation to form secondary particles (blue gold) is not essential for removal to the interface. We may therefore reasonably assume that the apparent immediate formation of a blue film from a red sol is also the result of coagulation of the gold *after* it had reached the interface, the aggregation of the gold being extremely rapid in such a case. A change from red to blue *at the interface* could actually be observed with Au_NB and Au_ZB and K_2CO_3. Immediately after shaking, the surfaces of the drops of emulsified amyl alcohol were seen to be covered with red gold, which changed to blue or bluish violet as the drops coalesced.

Other considerations made it appear very unlikely that the action of amyl alcohol on a Nordenson sol was due primarily to coagulation of the

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*Au_NB and Au_ZB had exactly the same appearance as Au_NA and Au_ZA. The former were made to more closely resemble one another than was the case with the latter, by decreasing the difference in the amounts of K_2CO_3 used in their preparation.

TABLE I

Effect of adding Sodium Hydroxide

Nordenson sol (B)			Zsigmondy sol (B)		
	Distribution			Distribution	
C	Interface	Aqueous layer	C	Interface	Aqueous layer
0.00	10BBl	0	0.00	0	10R
0.08	4B	6R	2.51	0	10R
0.25	1B	9R	5.02	+R	10−R
0.49	+B	10−R	7.53	+R	10−R
0.66	0	10R	10.04	1R	9R
0.82	0	10R	12.55	3R	7R
2.51	0	10R	17.57	5R	5R
5.02	0	10R	20.08	7R	3R
7.53	+R	10−R	25.10	9RP	1R
10.04	1R	9R	28.19	10RP	0
12.55	3R	7R	33.21	10BP	"
15.06	7BP	3R	35.72	"	"
20.08	10−BP	+R	38.35	"	"
25.10	10BP	0	51.35	"	"
30.70	"	"			
33.21	"	"			
35.72	"	"			

R = red B = blue BBl = blue black P = purple
BP = bluish-purple RP reddish-purple

The number indicates approximately the proportion of gold at the interface or in the aqueous layer. 10 represents the whole of the gold. The first fourteen Nordenson sols were red after twenty-four hours; the 15th and 16th had a tinge of purple and the 17th was bluish-purple. The first eleven Zsigmondy sols were red; the 12th and 13th had a tinge of purple; and the 14th was purple.

latter by water-soluble impurities in the former, the coagulum then being brought to the interface. It was established by experiment that methyl, ethyl, n-propyl and iso-propyl alcohols, obtained by the distillation of A.R. materials, had absolutely no effect upon Au_NA (or Au_ZA). The sharp distinction between miscible and immiscible alcohols can hardly be due merely to the absence in the one case and the presence in the other of ionising impurities. The matter was also put to the test in another way. A Nordenson sol was prepared from conductivity water which had been thoroughly shaken with a *large* quantity of purified amyl alcohol. The product, though purplish red in colour, proved to be very stable, showing no change in colour or sign of sedimentation after standing for several months. Viewed in the ultramicroscope it was seen to contain about equal proportions of green and red particles. There are two objections to the assumption that the larger particles were the result of coagulation by impurities in the alcohol. In the first place a very high rate of coagulation must necessarily be assumed, and rapid coagulation usually means complete coagulation. Secondly, the dissolved alcohol may quite well have decreased the rate of nuclei formation during the reduction, which would lead to coarsening of the gold. Even supposing, however, that coagulation had taken place, half the gold was still in the form of primary particles and these showed no tendency to aggregate. The sol was immediately shaken out with amyl alcohol, using the routine procedure.

The Influence of Electrolytes

As shown in the preceding section potassium carbonate and sodium hydroxide were found to oppose or promote film formation, depending upon the concentration. A number of other electrolytes were now tested to see how far these effects were general, exactly the same procedure being employed as formerly. The results are given in Tables II, III, and IV.

TABLE II

Nordenson sol (B)

Electrolyte	x	Distribution	y
KCl	2.4–26.8	At all concentrations gold completely removed to interface as blue, blue-black or blue film	7.3–9.8
$BaCl_2$	0.05–0.40		0.1–0.15
$LaCl_3$	0.0005–0.0049		0.0034–0.0039
HCl	1.4–14.3		5.7–7.2
KH_2PO_4	1.7–16.7		8.3–10.0
NaAc	4.2–41.9		12.6–16.7
$Na_2HPO_4/2$	5.0–50.0		25.0–30.0
$Na_3Cit/3$	7.5–75.0		30.0–37.5

The figures under x are the limits of concentration between which the action of the electrolyte was studied, and those under y, the concentration limits between which there appeared the first sign of change (blue tinge) in the sol, produced by the electrolyte alone in 24 hours. The concentrations are expressed in millimols per litre.

TABLE III

Zsigmondy Sol (B)

Electrolyte	Conc.	Film	y
KCl	2.4	1B	12.2–14.6
	4.9	8B	
	7.3	10B	
$BaCl_2$	0.1	1B	0.3
	0.2	3B	
	0.3	8B	
	0.4	10B	
$LaCl_3$	0.001	9B	0.0029–0.0039
	0.0018	10B	

TABLE IV
Zsigmondy Sol (B)

Electrolyte	Conc.*	Film	y
HCl	2.75	10BBl	5.51– 8.25
KH_2PO_4	1.70	10B	8.3 –10.0
Na Acetate	4.2	9B	20.8 –25.0
Na_3 Citrate/3	7.5	10B	22.5 –30.0
$Na_2HPO_4/2$	5.0	10B	20.0 –25.0

*Lowest concentrations employed.

These tables show that electrolytes in general promote film formation and that the concentration of electrolyte at which separation of the gold commences is always less, often very much less, than that (y) necessary to bring about a detectable change in the colour of the sol in 24 hours.

The influence of certain electrolytes was now more closely investigated employing an *acid* sol prepared by a modification of Zsigmondy's method. It was found possible to obtain perfectly clear, stable, yellowish-red sols by using tri-sodium citrate in place of potassium carbonate.** The following

TABLE V
Sol Au_{Cit}

	Distribution of gold					
	Na_3 Citrate		Na_2 phosphate		NaOH	
Conc. of electrolyte*	Interface	Aqueous layer	Interface	Aqueous layer	Interface	Aqueous layer
0.00	5B	0	5B	0	5B	0
0.25	3B	2R	+B	5-R	0	5R
0.50	2B	3R	+B	5-R	"	"
0.75	3B	2R	+B	5-R	"	"
1.00	5-B	+R	1B	4R	"	"
1.25	5B	0	1B	4R	"	"
1.50	"	"	2B	3R	"	"
1.75	"	"	4B	1R	"	"
2.00	"	"	5-B	+R	"	"
2.25	"	"	5B	0	"	"
2.50	"	"	5B	0	"	"
5.0					+R	5-R
7.5					3R	2R
10.0					5B	0
12.5					"	"
15.0					"	"
17.5					"	"
20.0					"	"

NaCl, HCl and KH_2PO_4 from 0.25 to 2.50: all gold went to interface at every concentration.

*Concentration of added electrolyte (in millimols per litre) after mixing with the sol.

**Anderson has prepared sols by using sodium citrate alone. Formaldehyde was employed in the present instance in order to approximate as closely to the Zsigmondy method as possible.

quantities proved satisfactory: 1 c.c. 0.6 percent chlorauric acid, diluted with 123.6 c.c. Bourdillon water, + 0.4 c.c. 0.1 M sodium citrate (Kahlbaum) + 3.0 c.c. 0.4 percent formaldehyde. On shaking 3 c.c. of this sol (Au_{cit}) with 1 c.c. of amyl alcohol the gold immediately collected at the interface, forming a blue film.

Table V summarises the results obtained by adding the various electrolytes. In these instances the sol + electrolyte mixtures did not stand for 24 hours but were treated after a few minutes. In no case was there any change in colour of the sol between mixing with the electrolyte and shaking with the alcohol. It will be seen from the table that, after sufficiently low concentrations, sodium citrate and secondary phosphate, as well as NaOH, exerted a stabilising influence upon the sol, whereas the other substances showed no tendency to prevent the gold from accumulating at the interface.

Determination of Particle Size

The average particle sizes of the sols Au_ZA and Au_NA were determined by a counting method which differed in some respects from the methods generally employed. The particles were fixed with gelatine. *accurate allowance being made for the optical heterogeneity of the latter* (*cf Tuorila*[8]).

Pieces of Coignet's "Gold Label" gelatine were cut from sheets chosen at random from a batch of thirty, and a 0.75% solution prepared from each piece, using optically empty conductivity water. Such solutions become very viscous at room temperature but do not set. On examination in the slit ultramicroscope they were found to contain a quantity of bright white particles, the number of which in a definite volume* was determined when the Brownian movement had been sufficiently reduced (by the cooling of the gelatine) to make counting easy. The field was effectively changed after each count by running out a drop of the solution from the ultramicroscope cell. The last column of Table VI gives the average number of particles contained in 3.09×10^{-6} cubic millimeters.

TABLE VI

Experiment	No. of counts	Av. no. of particles	
1	50	8.2	
2	30	8.0	
3	50	8.3	8.2
4	50	8.5	
5	50	8.0	

For counting experiments with a gold sol, 10 c.c. of the latter were mixed with 10 c.c. of 1.5 percent gelatine. Judging from their appearance to the naked eye and in the ultramicroscope neither Au_ZA or Au_NA was affected by this treatment. The gold particles were counted under the previous conditions of light intensity, etc. A fresh sample of gold-gelatine mixture was used for each experiment, and each count made on a different portion of the sample. The average radius of the particle was calculated by adopting the usual assumptions. Table VII contains the results.

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*Deliminated by means of a calibrated micrometer net. The dimensions of the net and the depth of the light beam were found by using a solution of fluorescein in the cell.

TABLE VII

Sol	Sample	No. of counts	Average number of particles			Av. radius of gold particles
			Total	In gelatine	In gold sol	
Au_ZA	1	15	40	8.2	31.8	30μμ
	2	22	41	”	32.8	30
Au_NA	1	35	19.6	”	11.4	42
	2	40	19.0	”	10.8	43
	3	40	19.5	”	11.3	42

The above method was used because when the sols were diluted for counts of the usual type, the background was found to be so dark, (indicating the absence of amicrons) that it was extremely difficult to distinguish the micrometer net. On the other hand if this difficulty was avoided by employing the sols at a sufficiently high concentration, it was impossible to make counts with any degree of accuracy unless the Brownian movement was considerably diminished. The method has also the advantage that the number of counts necessary is less than in the ordinary method.

Discussion

In agreement with the work of Zsigmondy, it was found necessary to purify carefully an organic liquid in order to ascertain with certainty if it possessed any action upon gold sols.* Employing organic liquids of the requisite quality, a pronounced specific action of the immiscible alcohols was shown to exist. Of all the liquids examined, they alone were found to affect Nordenson sols. Hence Zsigmondy's conclusion that acid sols are stable when shaken with organic liquids requires modification. It seems probable that this view was based on insufficient experimental material, since the only liquids mentioned as having been studied by him with regard to their influence upon acid sols, are benzene, toluene and ether.

The behaviour of a Nordenson sol when shaken with an immiscible alcohol is also obviously not in accord with Zsigmondy's statement that "Man kann allgemein sagen: reines kolloidales Gold ist stabil gegen Ausschütteln, koaguliertes** dagegen instabil." Moreover, as has already been indicated, the formation of red films provides very direct evidence that the primary particles of a sol may be attracted to the liquid—liquid interface without loss of individuality. It may however be argued that the contrast between e.g. Au_NA and Au_zA is due to a difference in primary particle size. While the actual size determinations appear to support this contention it is not possible without a closer study of the influence of electrolytes, to arrive at a definite conclusion as to the exact importance of the factor of particle size. Under certain circumstances at least, variations in the composition of the dispersion medium of the sol outweigh any effect of size. For example Au_NB was converted by suitable additions of alkali into a system closely resembling Au_ZB, which can hardly be due to an increase in the degree of dispersion.

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*Reinders[2] and Yanek[9] neglected to take this precaution and their results are correspondingly limited in value.

**i.e. aggregates (secondary particles) formed by the fusion of the original (primary) particles of the sol, which give a blue coagulum and appear red in the ultramicroscope.

In a recent paper Deutsch[10] suggests (1) that solid particles lower the interfacial tension between water and an organic liquid, (2) that the larger the particle the greater the capillary activity and therefore, (3) that the tendency of the particles to aggregate will be greater at a gold sol—organic liquid interface than in the sol itself, since this process reduces the free energy of the system. Thus, according to Deutsch, when a gold sol containing sufficient sodium chloride to produce minimum turbidity is shaken with hexane, the gold collects at the liquid-liquid interface because the coagulation is accelerated by the great increase in interfacial area created by the emulsification of the hexane, and since the coagulation is irreversible, the aggregated gold remains as a film between the two liquid phases after they separate. The absence of effect when a stable gold sol is shaken with hexane is explained in the following words: "die stärker geladenen, innerlich weniger abgesättigten Kolloidteilchen stärker durch das Wasser zurückgehalten werden als die durch Zusammentritt mehr abgesättigten aggregierten Teilchen" and "hier die Abstossungskräfte noch so stark wirksam sind, dass sie selbst an der Grenze noch zum Stabilisieren ausreichen, oder anders ausgedrückt, dass der Zuwachs an Capillaraktivität der durch Zusammentreten zweier Teilchen entstandener Aggregate noch immer zu klein ist, um eine Vergrösserung der Aggregationsgeschwindigkeit zu bewirken". There appear to be a number of difficulties in applying these views to the results of the present investigation. As has been repeatedly shown, a sufficiently acid sol is coagulated by amyl alcohol, although very stable in the ordinary sense. It might be assumed that the tendency to coagulate, while slight, was sufficient for the purpose, but the evidence suggests that the particles first collect at the interface and then coagulate. At least it is certain that in some cases the aggregation of the particles at the interface is, at the most, only of a loose nature (formation of red films). However it might still be assumed that such a species of aggregation constituted coagulation, or even that the electrical condition of the primary particles was not such as to counterbalance their capillary activity. Even supposing this to be the case, however, we have still to account for the absence of effect in the case of, for example, paraffin, which necessitates the further assumption that gold particles diminish the interfacial tension of water-alcohol to a greater extent than that of water-paraffin.

Moreover the coagulation, if such, resulting in the formation of a red film is in all probability reversible, as Whitney and Blake[12] have shown that precipitated red gold may be peptised.

It may be questioned, in any case, whether Deutsch is justified in assuming that the influence of the particles in the liquid-liquid interfacial tension is the factor of primary importance in the distribution of solid particles between two liquid phases. Apart from the difficulty of proving that such an effect exists, it does not seem reasonable to ignore the solid-liquid interfaces, even when dealing with the small particles of a gold sol. Regarding the problem as essentially one of "preferential wetting" the observations described in the preceding sections may be interpreted as follows. The alcohols are more strongly adsorbed at the surface of a gold particle than are the other organic liquids: this is concordant with the pronounced capillary activity of the alcohols. Hence the particles are more easily wetted by the alcohols and made to adhere to the organic layer. It is, however, to be expected that the adsorption of the alcohol molecules will be influenced by the electrical condition of the solid surface. As a rule organic substances depress the electrocapillary curve of mercury, their action being greatest in the neighbourhood of its maximum. This is ascribed to the effect of the electric field at the interface upon the adsorption of the organic molecules. That is to say, the adsorption is greatest when the field has some small value and decreases as the field becomes more positive or negative.[13] In this way it is possible to account for the influence of the nature of the dispersion medium upon the distribution of the gold particles when a gold sol is shaken with an immiscible alcohol, i.e. the effect of any electrolyte may be attributed to its influence upon the electrical charges of the particles.

If this view is correct we would expect to find much the same relationships holding as in the direct coagulation of a negative sol. This proves to be the case. In the first place the order of efficiency of the chlorides in promoting accumulation of the gold at the alcohol-water interface is $LaCl_3 > BaCl_2 > KCl$ (Table III). Secondly, those electrolytes ($NaOH$, K_2CO_3, Na_2HPO_4 and Na_3Cit) which oppose the action of the alcohol, have high coagulation values compared with potassium chloride (Tables I, II and IV).

It will be observed that the gold is not necessarily either completely brought to the alcohol-water interface or else left quite unaffected. All degrees of distribution are possible. This may be a size effect but another possible explanation is that the gold particles are not all equally charged, since Anderson[7], Garner and Lewis,[14] and Garner[15] found that they could account satisfactorily for the behaviour of gold sols when slowly coagulated by electrolytes, if they assumed that the primary particles carried unequal charges.

Since, of the salts examined only those which give alkaline solutions possessed the power of "protecting" a sol, the question arises as to whether this effect is due simply to decrease in the hydrogen ion concentration or is partly produced by adsorption of the salt anions. This problem is being investigated.

Summary

1. A considerable number of immiscible organic liquids have been examined with respect to their action on certain gold hydrosols.

2. Zsigmondy's conclusion that unambiguous results are obtained only if very pure liquids are employed has been confirmed.

3. It has been established that the immiscible alcohols exert a specific influence, since they may cause the gold of a stable sol to collect at the liquid-liquid interface.

4. The formation of red interfacial films under certain conditions has been observed.

5. The influence of various electrolytes upon the action of amyl alcohol has been studied.

6. It is suggested that the action of an immiscible alcohol is due to its strong tendency to be adsorbed at the surfaces of the gold particles and that the degree of adsorption depends upon the electrical condition of these surfaces. An electrolyte thus promotes or opposes accumulation of the gold at the interface according as it decreases or increases the particle charge.

References

[1] Zsigmondy: Nachricht. kgl. Ges. Wiss. Göttingen, Math-Phys. Kl., **1916**, 38. Also:—Z. anorg. Chem., **96**, 265 (1916); Z. Elektrochemie, **22**, 102 (1916); Zsigmondy-Thiessen: "Das kolloide Gold," 168 (1925).

[2] Reinders: Kolloid-Z., **13**, 235 (1913).

[3] Wiegner: Kolloid-Z., **8**, 227 (1911).

[4] Freundlich: "Colloid and Capillary Chemistry," 484 (1926).

[5] Nordenson: "Über die Bedeutung des Lichtes für die Bildung und Stabilität kolloider Lösungen." Diss. Upsala, 123 (1914). Also:—Svedberg "The Formation of Colloids," 70 (1921).

[6] Beaver and Muller: J. Am. Chem. Soc., **50**, 305 (1928).

[7] Anderson: Trans. Faraday Soc., **19**, 623 (1924).

[8] Tuorila: Kolloidchem. Beihefte, **22**, 191 (1926).

[9] Yanek: Ann. école mines Oural, **1**, 45 (1919).

[10] Deutsch: Z. physik. Chem., **136**, 353 (1928). See also:—Freundlich and Loebmann.[11]

[11] Freundlich and Loebmann: Z. physik. Chem., **139**, 368 (1929); Kolloidchem. Beihefte **28**, 391 (1929).

[12] Whitney and Blake: J. Am. Chem. Soc., **26**, 1339 (1904).

[13] Butler: Proc. Roy. Soc., **122A**, 399 (1929).

[14] Garner and Lewis: J. Phys. Chem., **30**, 1401 (1926).

[15] Garner: J. Phys. Chem., **30**, 1410 (1926).

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CATALYTIC EFFECT OF SOLVENTS. DECOMPOSITION OF MALONIC ACIDS

BY ROBERT E. BURK AND WILHELMINA DAUS

While numerous instances of the influence of solvents upon the velocities of chemical reactions have been investigated, some of those which have been most carefully worked through[1] have been addition reactions, e.g. the formation of substituted ammonium salts by the reaction of amines with alkyl halides, etc. In this type of reaction the possible factors which may contribute to the rate are not a minimum, e.g., there must be a third body present to carry off the heat of reaction[2] in order for reaction to occur, and the possibility that the heat of reaction would be dissipated internally in the case of complex molecules is not indicated in Menschutkin's work, since the more complex the molecules were, the slower the rates. That this factor is not the whole rate controlling one in these instances, is shown by the fact that Norrish and Smith found a discrepancy between the bimolecular collision rate of active molecules and the observed velocity, of 10^{-8} for the reaction between nitro-benzyl chloride and trimethyl amine in benzene, whereas the factor involving dissipation of heat of reaction could not in all probability lead to any such value, although it would be in the proper direction. Norrish and Smith consider every such collision between active molecules to involve at least one solvent molecule, and if this molecule were efficient in dissipating the energy of reaction, this required dissipation would not have to be considered at all. They attribute the discrepancy in collision and reaction rates to division of activation energy with solvent molecules at the moment of collision between active molecules.

Certain workers[3] on oxidation reactions in solution, however, in applying Christiansen's theory of negative catalysis[4] to such reactions, consider it not improbable that energized molecules of products may undergo of the order of 10^{-4} or 10^{-5} collisions with solvent molecules without losing their energy, and can transfer it specifically to "cold" reactant molecules at the moment of collision with them, without interference from solvent molecules of the type considered by Norrish and Smith.

With addition reactions of the above type, then, the solvent could affect the probability of loss of energy of activation at the moment of collision between active molecules, could lower the energy of activation, could dissipate energy of reaction, etc. Norrish and Smith were inclined to consider the effect of different solvents in altering the reaction rate as due to an effect upon the first factor. It seemed desirable to study a simpler reaction, such as a decomposition, in order that the factors influencing reaction rates in solution could be investigated more closely.

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[1] Menschutkin: Z. physik. Chem., **5**, 589; **6**, 41 (1890); Norrish and Smith: J. Chem. Soc., **130**, 129 (1930).

[2] Born and Franck: Ann. Physik, (4) **76**, 225 (1925).

[3] e.g. Bäckström: J. Am. Chem. Soc., **49**, 1460 (1927).

[4] Christiansen: J. Phys. Chem., **28**, 145 (1924).

The thermal decomposition of malonic acids was chosen because they fulfill this requirement, because they are important in themselves to organic synthesis, and because the influence of substitution of the active hydrogens on the decomposition rate could be compared with the influence of solvents. Work on the decomposition of acetone dicarboxylic acid has appeared[5] since the present research was started, and the decomposition of malonic acid itself has been investigated kinetically by Lindner,[6] by Hinshelwood,[7] and together with substituted malonic acids by Bernoulli and Wege,[8] by Bernoulli and Jakubowicz,[9] and by Jakubowicz.[10]

Experimental Procedure

The apparatus consisted of a thermostat containing a small reaction vessel of approximately 14 c.c. capacity. Temperature control to ±0.5°C. was obtained. Above the reaction bulb was sealed a vessel of 41.87 c.c. capacity, which was kept immersed in ice. This bulb was followed by a manometer, then a stopcock. All connecting tubing to this point was capillary. The stopcock led to an evacuating system with a discharge tube to indicate when a sufficient vacuum had been produced in the system. The reaction rate was followed manometrically by the pressure changes caused by the evolution of carbon dioxide due to the reaction:

$$RHC(COOH)_2 = RH_2CCOOH + CO_2$$

Due account was taken of the temperature differences of the two bulbs. When a solvent, which was somewhat volatile at the temperature of the reaction, was used, it distilled into the cold bulb and refluxed therefrom to the small bulb. Thus only its vapor pressure at 0°C. affected the manometer, and this was always too small to measure.

The sample was weighed out accurately before sealing on the reaction bulb, using the bulb as a weighing bottle. The amount of acid was so chosen that complete decomposition would not bring the pressure of carbon dioxide in the system above atmospheric. After the sample was weighed, (and the solvent added), the bulb was sealed onto the apparatus, and the system evacuated in order to evolve any dissolved or occluded inert gases.

The materials used were Kahlbaum's benzyl malonic acid (m.pt. 120.0°C.), ethyl malonic acid from E. Merck, Darmstadt (m.pt. 111.5°C.), and solvents the purest obtainable from Eastman Kodak Co. The oleic acid used was from Eastman Kodak Co. and was redistilled twice. The dimethyl aniline was also redistilled, but a redetermination with the distilled product showed no change in rate.

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[5] Wiig: J. Phys. Chem., **32**, 961 (1928); **34**, 596 (1930).

[6] Monatsheft, **28**, 1041 (1908).

[7] J. Chem. Soc., **117**, 156 (1920).

[8] Helv. Chim. Acta, **2**, 511 (1919).

[9] Helv. Chim. Acta, **4**, 1018 (1921).

[10] Z. anorg. allgem. Chem., **121**, 113 (1922).

Order of the Reaction

The kinetic order of the decomposition of benzyl malonic acid was determined by investigating the influence of initial concentration upon the time of half life using as a solvent palmitic acid, which was found to be without appreciable catalytic influence. Table I shows the independence of the time of half life and initial concentration for benzyl malonic acid.

TABLE I

Concentration (gms. in 5 cc. of acid)	Molality	Time for half change (min.)
1. 0.1046	0.1078	35
2. 0.2013	0.2075	31
3. 0.2516	0.2594	30
4. 0.3004	0.3097	29

The reaction is quite accurately monomolecular.

Influence of Various Solvents

Table II shows the half life for the decomposition of benzyl malonic acid in various solvents.

TABLE II

Decomposition of Benzyl Malonic Acid

Solvent	Half life (minutes) 125°C.	135°C.
None	75	(28.4)*
Oleic Acid	72	32.1
Palmitic Acid		31.0
ortho Nitrochlorobenzene		25.0
meta " "		22.5
para " "		26.0
Dimethyl Aniline	7	4.3

* This value is low, according to the temperature coefficient graph.

A remarkable independence of reaction rate and nature of solvent is evident. Determinations made with ortho, meta, and para nitrochlorobenzene indicate that the position of substitution in the benzene ring has no effect on the velocity, although accompanied by large changes in the electric moments of these molecules.[11]

One experiment was repeated in which about 100 mm. of carbon dioxide were added at the beginning to determine the effect of its presence on the rate of decomposition. It was found that the time of half life in this case was not appreciably different from the others.

All of this is in line with other monomolecular homogeneous reactions, which in the few cases investigated have been found to be less susceptible to catalytic influence than bimolecular reactions.[12]

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[11] Physik. Z., **30**, 391 (1929).

[12] This was pointed out by one of us (R.E.B.) at the Minneapolis meeting of the American Chemical Society, September 1929. Examples are the maintenance of decomposition rate of N_2O_5 (Lueck: J. Am. Chem. Soc., **44**, 757 (1922)), the racemization of pinene (Smith: J. Am. Chem. Soc., **49**, 43 (1927)), and the decomposition of acetone (Taylor: J. Phys. Chem., **33**, 1793 (1930)). For exceptions see Clusius and Hinshelwood: Z. Elektrochemie, **36**, 748 (1930).

It is to be observed that solvents having a considerable electric moment such as fatty acids and nitrochlorobenzenes have no catalytic influence. The malonic acids were not soluble in completely non-polar solvents such as purified mineral oil.

Dimethyl aniline was the only solvent of those investigated to show marked catalytic properties. Salt formation was indicated by a sharp rise in temperature when malonic acid was stirred with dimethyl aniline. However, reasons are given later for thinking that decomposition of the salt to free base and acid precedes the decomposition of the acid. The catalytic influence of this solvent was accompanied by a pronounced decrease in the temperature coefficient.

Effect of Substituting for the Active Hydrogens in Malonic Acid

This phase of the work was not investigated thoroughly because of its divergent nature, and of good correlation between such experiments as were made and previous rather extensive work. [10]A summary of results is given in Table III. Other comparisons will be made in discussing temperature coefficients.

TABLE III

Acid	Velocity Constant $\times 10^4$	Temperature (Centigrade)	Solvent	Observer
Phenyl malonic	104,921	100	water	Bernoulli and Wege
Benzyl malonic	1,968	100	water	" " "
Allyl malonic	1,321	100	water	" " "
Malonic	755	100	water	" " "
Malonic	477	100	glacial acetic acid	Linder
Diallyl malonic	649	100	water	Bernoulli and Wege
Methyl malonic	598	100	water	" " "
Ethyl malonic	508	100	water	" " "
Methyl ethyl malonic	322	100	water	" " "
Dimethyl malonic	297	100	water	" " "
Diethyl malonic	281	100	water	" " "
Monochlor malonic	1855	100	water	Bernoulli and Jakubowicz
Dichlor malonic	585	100	water	" " "
Tartronic	820	100	water	Jakubowicz
	half life (min.)			
Malonic	174	125	none	Hinshelwood
Ethyl malonic	148	125	none	Daus and Burk
Benzyl malonic	75	125	none	" " "

See Table II for benzyl malonic acid in various solvents.

Temperature Coefficients

Fig. 1 shows the results of plotting the reciprocal of the absolute temperature versus time of half life for the decomposition of benzyl malonic acid at various temperatures, without a solvent, in oleic acid, and in dimethyl aniline. The temperature coefficient determined by Hinshelwood[7] for malonic acid and that determined by Bernoulli and Jakubowicz[9] for malonic acid in water solution are also shown.

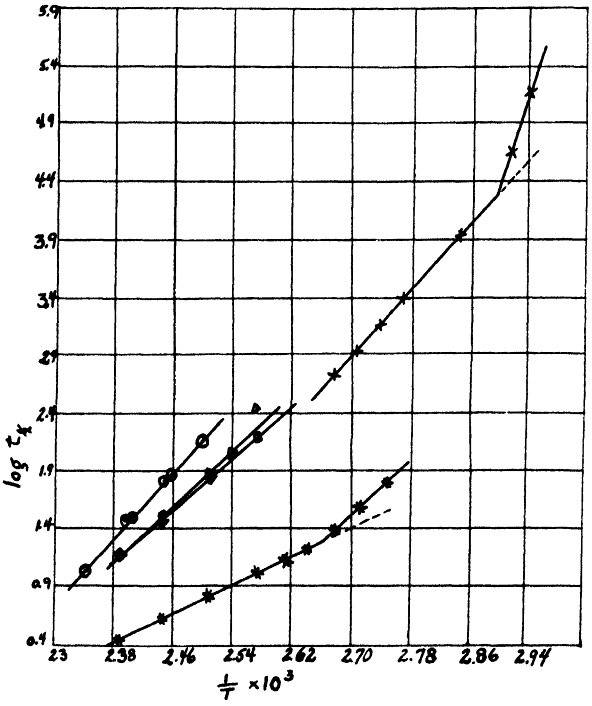

FIG. 1

△ Benzyl malonic acid, no solvent. Daus and Burk.

□ Benzyl malonic acid, solvent-oleic acid. Daus and Burk.

* Benzyl malonic acid, solvent-dimethyl aniline. Daus and Burk.

⊙ Malonic acid, no solvent. Hinshelwood.

× Malonic acid, solvent-water. Bernoulli and Jakubowicz.

It is to be observed that the point at 115°C. ($1/T = 0.002577$) for the decomposition of benzyl malonic acid without solvent is off the straight line in the sense of being too slow. This temperature was below the melting point of the acid. There was a marked induction period in the pressure change-time curve, there being a sharp acceleration when hydrocinnamic acid began to form in quantities sufficient to effect appreciable solution of the benzyl malonic acid. Thus the solid acid has a velocity constant of a lower order. A similar phenomenon was found by Hinshelwood[7] for the decomposition of solid malonic acid.

The energies of activation calculated graphically from the slopes are: 11,270 calories for the decomposition of benzyl malonic acid alone, 10,360 calories for the decomposition in oleic acid, which did not cause a marked increase in rate over the temperature range investigated, and 6,090 calories for the decomposition in dimethyl aniline between 105° and 145°C., which did have a marked catalytic effect. (The value calculated for the lower temperature range was 11,400 calories.)

The graphs leave no doubt that the marked catalytic effect of dimethyl aniline is accompanied by a definite decrease in the temperature coefficient.

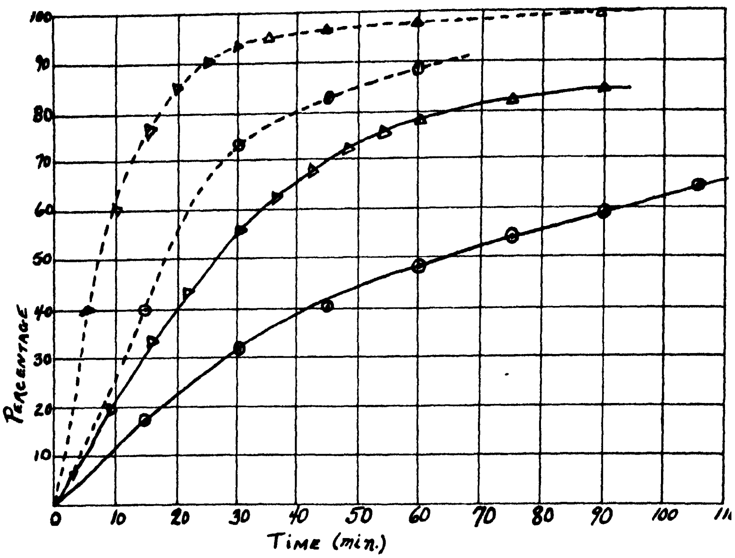

Fig. 2

—— ⊙ Percentage change of pressure with time at 90°C.
—— △ Percentage change of pressure with time at 100°C.
- - - ⊙ Percentage change of conductivity with time at 90°C.
- - - △ Percentage change of conductivity with time at 100°C.

It is seen that there is a change in slope in the sense of the reaction being too slow at the lower temperatures, beginning about 105° for benzyl malonic acid in dimethyl aniline. It was suspected that this was due to a dependence upon dissociation of the salt to free base and acid, which would lead to lower concentration of free acid and consequent diminution in rate.

In order to investigate this point conductivity measurements were made, using a small cell with platinum electrodes, and a Wheatstone bridge. Both high frequency alternating current with phones and electron tube amplification in the detecting arm, and direct current with a galvanometer in the detecting arm were used.

Fig. 2 shows the percent change in conductivity plotted against time at 90° and 100°C. The percent pressure change is also plotted against time for benzyl malonic acid in dimethyl aniline at the same temperatures. The fact that the conductivity would approach a value so small as to be immeasurable with our equipment shows that the end product, hydrocinnamic acid, has a negligible conductivity under these conditions. That the conductivity should drop to one percent of its original value at 90 minutes and 100°C., while the pressure change curve indicated that sixteen percent of the original benzyl malonic acid remained, showed that this acid also has a very small conductivity in dimethyl aniline under these conditions. These facts justify the conclusion that the observed conductivity is due almost entirely to the salt. The assumption of direct proportionality between conductivity and concentration of salt should also be justifiable as a first approximation.

TABLE IV

Temperature (°C.)	Half life in minutes		Temperature (°C.)	Half life in minutes	
	Salt decompn.	Acid decompn.		Salt decompn.	Acid decompn.
80	65.3	—	110	(1.85)	—
90	19.0	73.5	115	(1.084)	10.2
95	(10.24)	38.5	125		6.8
100	7.5	26.0	135		3.9
105	(3.236)	17.2	145		2.6

Table IV shows a comparison of half lives of decomposition of the salt to free base and acid and of the acid to hydrocinnamic acid and carbon dioxide. The values in brackets are calculated from the temperature coefficient as determined from the measured points, which lay on an excellent straight line when log $t_{1/2}$ was plotted against $1/T$.

Fig. 3 shows the values of the time of half change in conductivity plotted against the reciprocal of the absolute temperature with the corresponding half pressure change values for the decomposition of benzyl malonic acid in dimethyl aniline as solvent and without a solvent. It is clear from the table and graphs that the rate of salt decomposition becomes very rapid compared with the acid decomposition at a point corresponding to that at which the temperature coefficient of the acid decomposition settles out to new and lower, but constant value. Furthermore the temperature coefficient for this reaction at low temperatures tends to assume the corresponding value for the salt decomposition.

With concurrent reactions, that reaction having the higher temperature coefficient may predominate at higher temperatures in case it is homogeneous, and that with the lower temperature coefficient is heterogeneous[13]

This phenomenon depends upon the reaction with the lower temperature coefficient being heterogeneous, in which case but a small proportion of the total reactants is undergoing heterogeneous reaction at a given instant.

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[13] This type of composite reaction is discussed by Hinshelwood: "Kinetics of Chemical Change in Gaseous Systems," 2nd edition, p. 45. Examples are the combination of hydrogen and sulfur (Norrish and Rideal: J. Chem. Soc., **123**, 696 (1923)) and the decomposition of hydrogen iodide in pyrex (H. A. Taylor: J. Phys. Chem., **28**, 984 (1924).)

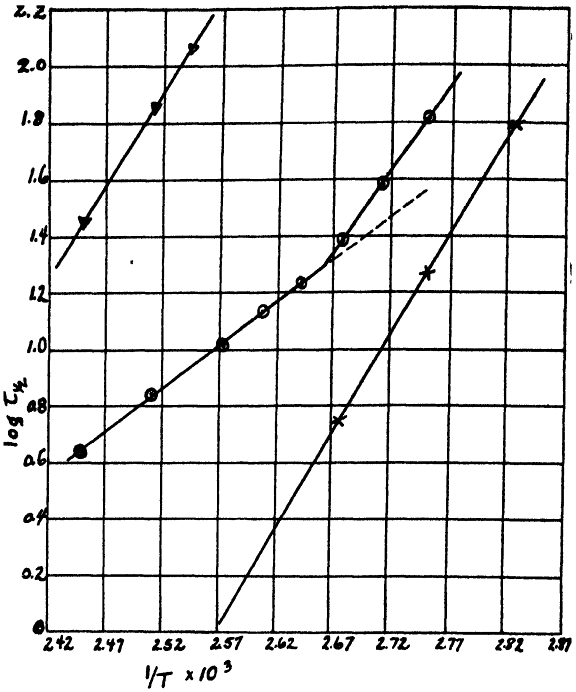

Fig. 3

△ Benzyl malonic acid, no solvent.
⊙ Benzyl malonic acid in dimethyl aniline.
× Conductivity due to salt.

This behavior would not be found with two homogeneous reactions of the same type, for if their velocity expressions were:

$$1.\ k_1 = p_1\, e^{-A_1/RT} \qquad\qquad k_1 = p_1 n_1 e^{-A_1/RT}$$
$$\text{or}$$
$$2.\ k_2 = p_2\, e^{-A_2/RT} \qquad\qquad k_2 = p_2 n_2 e^{-A_2/RT}$$

where p is a probability factor
k is the velocity constant
n is the number of collisions per second
A is the energy of activation.

If p_1 and p_2, and n_1 and n_2 are not greatly different, then if $A_1 < A_2$, reaction (1) will always exceed reaction (2) in speed in spite of a relative increase in the speed of (2).

With consecutive reactions, as in our case, the reaction with the lower temperature coefficient not only increases in speed relative to the other, but likewise predominates as the temperature is increased.

It is seen in Fig. 1 that in the results of Bernoulli and Jakubowicz, there is likewise a falling off in the rate of decomposition of malonic acid in water at the lower temperatures. Here salt formation is out of the question. However, since these temperatures are far below the melting point of malonic acid, association of these molecules may occur, leading to a diminished reaction rate for the complexes, as was found for the solid malonic acid by Hinshelwood, and for benzyl malonic acid by us.

Any residual effect due to incomplete salt decomposition at the higher temperatures could only make the temperature coefficient appear higher than its true value, so that the conclusion that the temperature coefficient is lowered by the catalyst cannot be jeopardized. Such demonstrations of temperature coefficient lowering with catalysis, though suspected, are not frequent in the literature.[14]

Interpretation of the Lowering of the Temperature Coefficient

A great deal of evidence has been accumulated to indicate that a major action of catalysts is a lowering of the energy of activation, the dominant factor governing reaction rates.[15] An interpretation which has been given to this is that it may be brought about under proper conditions by the stretching of bonds by a particular kind of association between catalyst and reactant involving more than one point of contact, a point of view which has been shown to be in excellent agreement with those phases of catalysis previously most difficult to explain, namely specificity, and promoter action.[16] The preponderance of evidence was in favor of this type of distortion rather than the atomic distortion mechanism[17] for the influence of a catalyst upon a bond. Recent work on band spectra,[18] and particularly upon Raman Spectra,[19] tends to minimize the possibilities of the atomic distortion mechanism. Some new suggestions arise from Quantum Mechanics, according to which the principal component of non-polar bonds is the resonance or exchange force arising from a coupling of the spin moments of unpaired electrons in the respective atoms making up the bond, such a force being demanded by one of the solutions of Schrödinger's wave equation, resulting from an exchange of the two electrons which potentially can form a bond.[20]

According to London[21] the following notions regarding chemical activation result. If we have a pair of atoms forming a non-polar bond and a third atom approaches which is capable of "resonance" combination with either of the two atoms forming the bond, the bond will be weakened, and if the potential reaction is exothermic the new combination will be effected, and the second atom which was a part of the original bond ejected. However, the third atom experiences a repulsion before approaching sufficiently closely to cause the phenomena just described. The energy of activation would thus be that necessary to overcome this "potential wall" in the case of exothermic "atom" reactions, and has been found by Polanyi and co-workers[22] to be vanishingly small for reactions of the type:

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[14] Some new cases, e.g., the decomposition of ethers catalyzed by halogens and organic halogen compounds have recently been reported. (Clusius and Hinshelwood: Z. Elektrochemie, **36**, 748 (1930) Summarizing paper.).

[15] See e.g., Hinshelwood: "Kinetics of Chemical Changes in Gaseous Systems," 2nd Edition; Burk: Sixth Report of the Committee on Contact Catalysis, J. Phys. Chem., **32**, 1601 (1928).

[16] See Burk: J. Phys. Chem., **30**, 1134 (1926); **32**, 1601 (1928); Balandin: Z. physik. Chem., **B2**, 289 (1929).

[17] See, e.g., Langmuir: Trans. Faraday Soc., **17**, 610 (1922).

[18] See Burk: Sixth Report (Loc. Cit.) for a partial summary.

[19] See e.g., Smekal: Z. Elektrochemie, **36**, 618 (1930); Andrews: Phys. Rev. (2), **36**, 546 (1930).

[20] Heitler and London: Z. Physik, **44**, 455 (1927); Rouark and Urey: "Atoms, Molecules and Quanta," p. 684 (1930); Heitler: Physik. Z., **31**, 186 (1930); Mulliken: Chem. Rev., **6**, 536 (1929). This relatively simple concept seems, however, to be growing more complex, because of a "degeneration" of orbital momentum of electrons as well as of the spin moments leading to binding forces of the same order of strength. (Heitler: Naturwissenschaften, **17**, 546 (1929)).

[21] Z. Elektrochemie, **35**, 552 (1929).

$$AB + C = AC + B + \text{energy}$$

London then says, p. 553, "If the distance between the atoms of the original bond is increased, as by increase in vibration or through the influence of a nearby catalyst, the resonance repulsion against the approach of the third atom will be weakened, and the height of the potential wall lowered."

This, in common with previous concepts,[23] attributes the activation process to increasing the distance between the atoms of the bond concerned. However, in contradistinction, the energy of activation as seen by London is external, i.e., the energy necessary to overcome the potential wall rather than the remaining energy necessary to break the bond (for exothermic reactions).

In case the reaction is endothermic, the heat of reaction per molecule must be added to that necessary to overcome the potential wall in order to have a successful elementary act of reaction.

The small activation heats of atomic reactions are attributed by London to the existence of "sensitive spots" on the diatomic molecule easily reached by the approaching atom. For a reaction of the type:

$$XY + ZW = YZ + XW$$

both X and Y cannot reach the sensitive spot of ZW, etc., so activation heats of higher order result, which London says should be close to the energy requirements of:

$$(1)\quad XY + ZW = YZ + X + W$$

or

$$(2)\quad XY + ZW = XW + Y + Z.$$

This works out excellently with the homogeneous bimolecular reaction:

$$2HI = H_2 + I_2 \quad \text{Energy of activation, 44,000 calories}^{24}$$

$$H_2 = 2H - 98{,}100 \pm 2{,}300 \text{ calories}^{25}$$

$$I_2 = 2\,I - 35{,}600 \pm 70 \text{ calories}^{25}$$

$$HI = H + I - 66{,}000 \text{ calories (spectroscopic data)}^{26}$$

$$HI = H + I - 69{,}300 \text{ calories (thermal determination)}^{26}$$

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[22] Beutler and Polanyi: Z. physik. Chem., **B1**, 3; Bogdandy and Polanyi: 21; Polanyi and Schoy: 30; Outuka and Schoy: 62 (1928).

[23] Burk: J. Phys. Chem., **30**, 1134 (1926).

[24] Lewis: J. Chem. Soc., **113**, 471 (1918).

[25] Franck: Z. Elektrochemie, **36**, 587 (1930).

[26] Sponer: Z. Elektrochemie, **34**, 488 (1928).

$2HI = H_2 + 2I - 34{,}900$ calories if the spectroscopically determined heat of dissociation of HI is used, and 40,500 calories if the thermally determined value is used

$2HI = I_2 + 2H$ gives the wrong order of values for the heat of activation.

Polanyi[27] in applying these principles to activation at surfaces, considers again that activation involves stretching of bonds, and in still closer analogy to pre-quantum mechanical concepts, considers that activating adsorption of a molecule AB involves two surface atoms; surface complexes are formed in which the bond AB is either stretched or broken, and the bonds catalyst-A and catalyst-B must of course be of such strength that they lead to increased reaction rates. The correlation with London's "sensitive spot" concept is not so lucid. If the catalyst atoms are spaced somewhat farther apart than the atoms of AB, and we have two point adsorption, then clearly the resonance weakening of the bond would be assisted by mechanical stretching.[28]

The most recent contribution of quantum mechanical theory to the concepts of factors participating in catalytic activation is due to Born and Franck,[29] and has been but very superficially revealed. Referring to the association of energy of activation with that required to overcome a potential wall, they say that if on a catalyst the reacting molecules can be held at a distance from each other comparable with the distance reached in a gaseous collision, and for a time long compared with the duration of a gaseous collision, there is a certain probability of reaction although the energy necessary to overcome the potential wall is not present. This probability depends upon the height and breadth of the potential wall, and upon the mass of the atoms, and is exceedingly sensitive to distance apart at which the atoms find themselves as a result of adsorption and to the time during which they are held in this position. This point of view emphasizes once more the correlation between the spacing of catalyst atoms and their specific action, which various chemists have sought to bring out.[30] However, the energy of activation which is found for catalytic reactions from this viewpoint presumably would be due to the energy requirement for the adsorption of the reactants in the sensitive configuration, in case the reaction probability is itself independent of temperature, although the previously described processes could go on simultaneously and involve temperature coefficients.

The energy of activation may thus be: (1) that which is required for the heat of reaction in the case of endothermic reactions (including in this class the first step of exchange reactions, e.g., $XY + ZW = XZ + Y + W$), (2) that required to overcome a potential wall, (3) that required to produce a sensitive configuration on a surface. In catalysis, then, either (1) or (2) (principally (1)?) is lowered as compared with the homogeneous values, or (3) is substituted.

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[27] Z. Elektrochemie, **35**, 561 (1929).

[28] Cf. Burk: J. Phys. Chem. **30**, 1134 (1926).

[29] Z. Elektrochemie, **36**, 588 (1930).

[30] e.g. Emil Fischer in his lock and key concept of the specificity of enzymes; Adkins and coworkers: J. Am. Chem. Soc., **45**, 809 (1923); **46**, 130, 2291 (1924); Burk: Loc. cit.; Balandin: Loc. cit.

Just what the activating mechanism is, for dimethyl aniline on benzyl malonic acid, is a matter of speculation. The principles developed for heterogeneous catalysis may be used in the main for homogeneous catalysis, and a large organic molecule as a catalyst, gives plenty of opportunity for spacing effects, etc. The catalytic action is probably dependent, however, upon the "free valencies" of the nitrogen in the present case. Furthermore, since the salt has been found to be less reactive than the free acid, the carboxyl hydrogen atom is probably involved in the first elementary act. The activation may consist in a mild excitation of the electron taken up from the hydrogen atom by the carboxyl group leading to dissociation of the carboxyl into neutral hydrogen and free RCHCOOH COO radicals;[31] this would be a still different type of activation. This may be catalyzed by dimethyl aniline if the nitrogen of the aniline gives up an electron to the hydrogen ion, and then takes one again from the carboxyl ion, in case these two energy steps are appreciably smaller.

There are no evident unpaired electrons in dimethyl aniline available for quantum mechanical coupling which might loosen the OH bond of a non-ionic form of the free acid through resonance action, although a collision with an acid molecule might render them available for coupling so that the dimethyl aniline could fulfill its catalytic duty of bond loosening in the quantum mechanical sense. That there is a type of quantum mechanical perturbation which does not depend on unpaired electrons is indicated in London's new interpretation of van der Waals' forces.[32]

That secondary valence forces have much to do with the present case is, however, not indicated since most solvents, including some which are quite polar, have little influence.

With respect to the effect of replacing the hydrogen atoms alpha to the carboxyl groups by other groups, there is no certain evidence of a lowering of the heat of activation, though a slight lowering is indicated when one benzyl group is introduced, and the rate is certainly increased. A plot of Bernoulli and Jokubowicz' values showed that only their work on malonic acid gave a good straight line when 1/T was plotted against log k, the data for the other acids being erratic.

It has been said that on account of results from investigations of band spectra and Raman spectra, effects corresponding to a distortion carried through the chain should be minimized. This is confirmed by the observation of Bernoulli and Jakubowicz[9] that when both alpha hydrogens are replaced by like substituents the decomposition rate is less than for malonic acid alone, in all cases. Whereas when only one is substituted, the decomposition rate is greater, for phenyl, benzyl, allyl, chlorine and hydroxyl. This would scarcely follow if the effect of substitution on decomposition rate were due to distortion carried through the chain. Furthermore, the halogen substituted acids did not decompose particularly rapidly. This is contrary to the effect of halogen substitution on the strength of acids. This, however, may be a space effect rather than a chain effect.[33]

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[31] See Franck: Loc. cit., for such processes of dissociation induced photochemically in polar unions.

[32] Z. Physik, 63, 245 (1930).

Since in solution there would always be enough activating collisions to maintain the Maxwellian distribution of energy between acid molecules, the reaction rate would not fall off with diminished concentration and the number of participating internal degrees of freedom cannot be calculated. The heat of activation, reaction rate, and temperature coefficient do, however, fall into line fairly well with other monomolecular reactions.[34]

Summary

The decomposition rate of malonic acids, especially benzyl malonic acid, have been determined both for the acid alone and in various solvents.

Dimethyl aniline was the only solvent, of those investigated, to show marked catalytic action. This was accompanied by a definite lowering of the temperature coefficient. The effect was shown not to be due to salt formation.

Possible mechanisms for activation by the catalyst have been discussed.

Morley Chemical Laboratory,
Western Reserve University,
Cleveland, Ohio.
December, 22, 1930.

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[33] This is suggested by the work of McInnes: J. Am. Chem. Soc., **50**, 2587 (1928).

[34] See Hinshelwood: "Kinetics of Chemical Changes in Gaseous Systems, 2nd. Ed., p. 159. The reaction rate of N_2O_5 in Hinshelwood's table would be too high for the purposes of the table if a chain mechanism applied to this case.

LIESEGANG RINGS

BY OLIN F. TOWER AND EDNA E. CHAPMAN

In 1928 Hedges and Henley[1] published a paper, in which they showed that in many cases Liesegang rings can be obtained by a process of coagulation. For example, they prepared a colloidal solution of silver chromate in gelatin, covered it with silver nitrate solution, and thereby obtained rings of silver chromate very similar to those of the original Liesegang experiments. They also found that it was not necessary for the diffusing electrolyte to possess an ion in common with the salt to be coagulated. By allowing a solution of aluminium sulfate to diffuse into a colloidal solution of arsenious sulfide in gelatin, rings of arsenious sulfide were obtained.

Rings of cadmium sulfide and zinc sulfide had already been prepared in this laboratory by the usual method.[2] Experiments were therefore undertaken to see whether rings of these substances could be obtained by the method described by Hedges and Henley. Colloidal solutions of cadmium sulfide were prepared by mixing a tenth-normal solution of cadmium chloride in agar-agar solution with a tenth-normal solution of ammonium sulfide. On standing, these give a very good colloidal solution of cadmium sulfide. More concentrated solutions than these could not be used, as a precipitate of cadmium sulfide was then obtained. Above several of these colloidal solutions of cadmium sulfide in agar-agar were placed cadmium chloride solutions of 0.5% concentration and regularly increasing concentrations up to 20%. These were allowed to stand for several days, but no rings of cadmium sulfide were obtained. Neither were rings obtained when the supernatant liquid contained ammonium sulfide, ferric chloride or aluminium sulfate. The method described by Hedges and Henley is, therefore, not a general one, and only appears to yield rings in certain special cases.

In continuation of the work referred to above by Daus and Tower, we here wish to report the results of experiments of preparing Liesegang rings of manganese, nickel and cobalt sulfides. In all these cases a method similar to that used before was followed. The electrolyte containing the sulfide ion was placed in the gelatinous medium, which consisted sometimes of gelatin, and sometimes of agar-agar, and the electrolyte containing the metallic ion was placed in the supernatant liquid. With gelatin the sulfide ion was furnished by ammonium sulfide, as the gelatin did not set when containing sodium sulfide. With agar-agar either ammonium sulfide or sodium sulfide could be used. The best concentrations of sulfide ions were found to be between 0.2 and 0.5 normal, and for the manganese ion between 0.1 and 2 normal. It

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[1] J. Chem. Soc., **130**, 2714 (1928).

[2] Daus and Tower: J. Phys. Chem., **33**, 605 (1929).

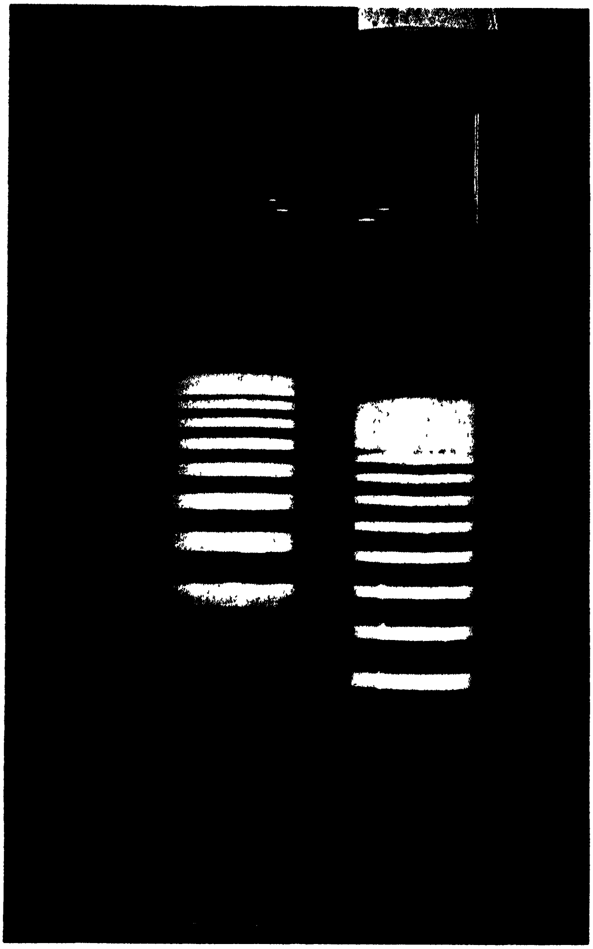

FIG. 1

0.3N $MnCl_2$ 0.9N $MnCl_2$

0.4 $(NH_4)_2S$ 0.9N $(NH_4)_2S$

made no difference whether manganese chloride or sulfate was used. Rings obtained with manganese chloride and ammonium sulfide are shown in Fig. 1.

In attempting to form rings of nickel and cobalt sulfides, it was found that no bands were obtained when ammonium sulfide was present in the gelatinous medium. The only bands that were obtained were, therefore, with sodium sulfide in agar-agar, and the supernatant liquid containing either the chloride or sulfate of either nickel or cobalt. The best concentrations for the sodium sulfide were 0.4 to 0.6 normal, and for the nickel or cobalt salt 0.7 to 2.0 normal. These rings were much finer and closer together than those with manganese sulfide, as is seen in Fig. 2.

Assumptions as to the way in which these rings are formed have already been given in the previous article, and we find no reason to modify them here.

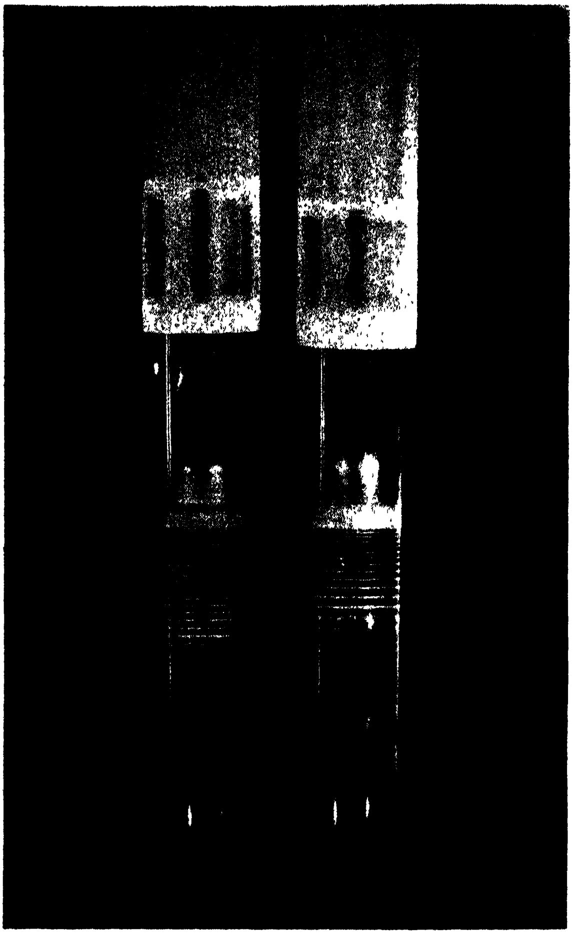

FIG. 2

$0.19N\ NiCl_2$	$0.7N\ NiCl_2$
$0.6N\ Na_2S$	$0.6\ Na_2S$

Summary

This paper records experiments to show that the method of forming Liesegang rings by coagulation, as recorded by Hedges and Henley, does not apply in all cases.

Methods for preparing Liesegang rings of manganese, nickel and cobalt sulfides are given.

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Cleveland, Ohio.

ON THE COMPOSITION OF ACID BORIC ACID-DIOL COMPOUNDS

BY J. BÖESEKEN AND N. VERMAAS

Introduction

For some time the Boric Acid Problem has been studied according to different physical methods in the Laboratory of Organic Chemistry at Delft. The article by Wilder D. Bancroft and Herbert L. Davis,[1] whose conclusions depart entirely, not only from the results obtained at Delft during the last few months, but also from all that had already been attained before by one of us and his pupils and by several other investigators, induces us to publish some of our results now.

Before proceeding to the discussion of the cause of the variation of acidity, we may be allowed to draw attention to a few passages of this paper which are, in our opinion, incorrect, or which, through their incompleteness, leave room for an erroneous conclusion.

On the significance of the preparation of optically active BR_2-anion (R = diol radical) by which the proof is furnished not only of the *existence* of these complexes, but also of their configuration, no more is said than the sentence: "One of the most recent developments in this field is the isolation of substances which appear to be compounds in which boron must be assumed to have a coordinated valence of four and to possess optical activity," while on p. 2482 it is stated that "the isolation of these compounds seems to be attended with some difficulties," whereas in reality a number of these compounds has been isolated without any difficulty, if in the polyols the hydroxyl groups are favourably situated, and the salts are not too readily soluble in water or in salt solutions.

When we consider that these salts are obtained from aqueous solutions it is natural to assume that the anions BR_2 are also present in aqueous solutions and to ascribe the increase of the conductivity of boric acid by the polyols to the formation of complex acids.

Referring to what will follow presently, where we have also furnished the proof of the existence of these anions in aqueous solution we may point out that these complex acids will be *very strong* acids, because they are formed by absorption of the electron of the H-atom, through which in the completely formed compound the hydrogen will be present entirely as proton; in aqueous solutions these acids will, however, be hydrolysed for an important part; hence it is to be expected that the free acids HBR_2 could be isolated from their aqueous solutions only if they should be much less readily soluble than boric acid or the other component, and there is not much chance of this, exactly with these strong acids.

We meet here with analogous circumstances as with the ammonium-bases, which must cede an electron to the hydroxyl group and which are in consequence very strong bases. These can, indeed be isolated, if no H-atom is bound to the N; if this *is* the case they are dissociated for the greater part in aqueous solution, making the impression of being weak bases.

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[1] J. Phys. Chem., **34**, 2479 (1930).

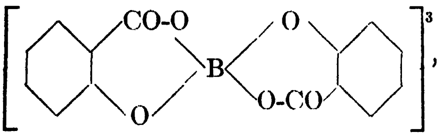
It is, accordingly, not astonishing that Bancroft and Davis have not succeeded in isolating complex acids, and notably not with glycerine, where the acid is almost completely hydrolysed (p. 2486).

As here the formation of strong acids is in question, the reactions, just as when the equilibrium amine + $H_2O \rightleftarrows$ ammonium base is established, will bear the character of ion reactions, hence take place practically instantaneously. We may, therefore, by no means compare the establishment of the equilibrium: 2 diol + boric acid $\rightleftarrows$ complex + H_2O with the formation of esters of alcohols with weak organic acids (p. 2468 and conclusion 6 pp. 2505-2506).

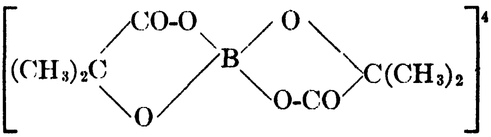
In consequence of the fact that these complexes and notably glycerine boric acid, remain almost entirely hydrolysed, the heat effect will be slight (2486). Glycerine happens to be a very unfavourable object to prove the formation of compounds by another way than by the increase of the conductivity.

Meulenhoff[2] has succeeded in preparing free dipyrocatecholboric acid by heating its dry aniline salt in vacuo; in this it is noteworthy that the acid itself is very little volatile, as may be expected from such a molecule with polary bonds; it carbonizes at 200°.

We have succeeded in splitting up *three* types of these compounds into optical antipodes, viz. the anions:

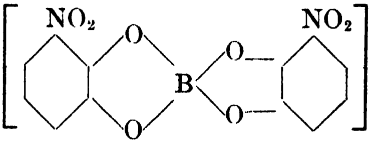


[3],



[4]

and



[5]

by precipitating them from *aqueous* solutions with optically active bases.

The spirane configuration of these compounds and the presence of these complexes also in aqueous solutions can, therefore, hardly be called in question. As we have exactly proved the existence of the anions BR^-_2 (as well as of BR^-) in aqueous solutions, as will be set forth presently we will pass by Bancroft and Davis's other considerations in silence.

We will only point out that the tartaric acids form a complicated case, because compounds of boric acid are possible both with the two α-hydroxy-carbonic parts of the molecule, and with the middle glycol part. This is one of the reasons why the esters and the amides of the tartaric acid have been examined, where we have only to do with the glycol part of the acids. Here, too, it was found that the active compounds had a greater influence on the conductivity than the inactive ones, which can be explained by the stronger mutual repulsion of the COOR ($CONH_2$) groups than that of the OH-groups, owing to which these latter will lie closer together in the active acids than in the inactive acids. We may add to this that in the imides, where in consequence of the formation of the 5-atomic ring, the position of the OH-groups is fixed, the very reverse is to be expected, and has also been found by J. Coops.[6]

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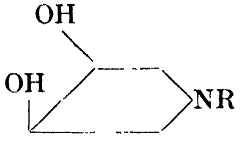
[2] Doctor thesis, Delft, pp. 35-36 (1924).

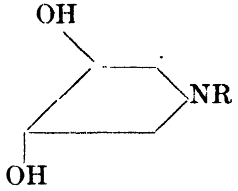
[3] Meulenhoff: Z. anorg. allgem. Chem., **142**, 377-379 (1925).

[4] Böeseken, Müller and Jap Hong Jouw: Rec. Trav. chim., **45**, 919 (1925).

[5] Böeseken and Mijs: Rec. Trav. chim., **44**, 750 (1925).



Anti-tartaric-imide



act-tartaric-imide

The anti-tartaric acid imide causes a considerable increase of the conductivity of the boric acid, the act-tartaric acid imide *absolutely* none. We do not see very well, how this difference can be accounted for in another way than by the formation or non-formation of compounds with boric acid. If Bancroft and Davis should rest satisfied with "the fact that the boric acid *dissolves* preferentially in the activating substance and is therein more highly dissociated than in water" this purely physical formulation does not seem satisfactory to us, and the assumption of a compound with the favourably situated hydroxyl groups of strongly acid character in the first case, the formation of which is impossible in the second case, seems very much more rational.

As regards the tartaric acids themselves, the separation of the potassium boro tartrate KBT_2 with two tartrate groups by Lowry[7] is so important, because it shows so convincingly how easily, with a favourable position of the hydroxyl groups, a compound of the spirane type is formed; accordingly we readily leave it to the readers to decide whether they will accept this formula given by Lowry, or that given by Bancroft and Davis on p. 2502.

In conclusion we will point out, that the summary given on pp. 2495-2496 of investigations of one of us and his pupils, is very incomplete for which reason we may lay aside their opinion on the small value of our investigations with a view to configuration determinations.

Let us now proceed to the closer examination of aqueous solutions of boric acid and polyols.

Bancroft and Davis hold the view that "the activation of boric acid in the presence of sufficient glycerine or mannite or certain other substances, is not

[6] Doctor thesis, Delft, pp. 62-67 (1924).

[7] J. Chem. Soc., **1929 II**, 2853.

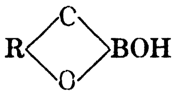
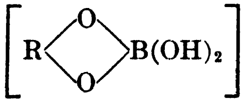
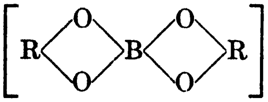
due to compound formation, but to the fact that the boric acid dissolves preferentially in the activating substance, and is therein more highly dissociated than in water".

Among other things the writers also make the following remarks: "The phenomena studied by Böeseken do not require such a ring structure as he adopted, but may more probably be due to a kind of complex formation involving only one hydroxyl group, the adjacent carboxyl, hydroxyl, or keto groups being required to activate the one reacting with the boric acid.

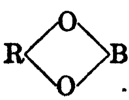
As evidence against the hypothesis of compound formation in these systems is the fact that there is no indication of the existence of a solid compound in the phase study of their aqueous solutions. This is true of the mannite system as well as of the tartaric acid systems, although mannite is one of the most effective activators of boric acid, and should give a compound if one exists."

It will now first be briefly discussed to what the acidity of boric acid diol solutions is to be attributed, after which in the conclusion Bancroft and Davis's views will be tested by the obtained results.

General Remarks on Boric Acid Diol Complexes

When a "favourable" diol (α-oxy-acids etc. included) is added to a solution of boric acid in water, the ring compound  is primarily formed, which, on account of the tendency of boric acid to assume the pentavalent condition, can pass into resp. the monobasic acids H  and H  with water or with a new molecule of diol.

These acids are comparatively strong, and as regards structure perfectly analogous to the acid $H[B(OH)_4]$ to which at present the acidity of a boric acid solution is ascribed.[8,9]

With less favourable diols the position in space of the OH-groups will render the transition of boron to the tetrahedric valence arrangement almost impossible; hence the complex formation will go no further than the , and no increase of acidity will be observed (2-4 dimethyl pentane -2-4 diol boric acid.)[8]

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[8] Hermans: Z. anorg. allgem. Chem., **142**, 83 (1925).

[9] Böeseken and Coops: Rec. Trav. chim., **45**, 407 (1925).

With absolutely unfavourable diols no complex formation will take place at all.

Combining all the undissociated complex compounds under HBR and HBR_2, the course of the reactions may be represented as follows:

$$\text{HB (boric acid)} + \text{R (diol)} \rightleftarrows \text{HBR} \rightleftarrows \text{H}^+ + \text{BR}^-$$

$$\text{HBR} + \text{R} \rightleftarrows \text{or}$$

$$\text{HB} + 2\text{R} \rightleftarrows \text{HBR}_2 \rightleftarrows \text{H}^+ + \text{BR}^-_2.$$

On the assumption that HBR and HBR_2 are strong acids, HBR and HBR_2 may be neglected with respect to their ions in the case of favourable diols in diluted solution.

The condition of the solution is then determined by the following equilibrium constants:

$$k_1 = \frac{(\text{H}^+) \times (\text{BR}^-)}{(\text{HB}) \times (\text{R})} \text{ and } k_2 = \frac{(\text{H}^+) \times (\text{BR}^-_2)}{(\text{HB}) \times (\text{R})^2}$$

These constants are analogous to those of carbonic acid and ammonia.

If for less favourable diols HBR and HBR_2 may possibly not be neglected, very certainly these equations cannot be used for more concentrated solutions, because then on one side tetra-boric acid[10] on the other side the undissociated HBR and HBR_2 may begin to play a part also for the favourable diols.

By division of the equilibrium constants we get:

$$1) \ldots\ldots\ldots\ldots \frac{[\text{BR}^-_2]}{[\text{BR}^-]} = \frac{\text{K}_2}{\text{K}_1} \times [\text{R}]$$

If now K_2/K_1 is $= \pm 10^3$ and the diol concentration is ± 0.1 mol., then (BR^-_1) may be neglected with regard to (BR^-_2) and the acidity of such a boric acid diol solution is governed by the di-complex.

Poly-alcohols

For poly-alcohols this has been proved in the Rec., **49**, 711, to which we refer here, as also to the theoretical derivations. Inversely it has appeared from this, that actually $K_2/K_1 = \pm 10^3$ or $> 10^3$. To the measurements mentioned in Rec., **49**, 711 only some results are added calculated from measurements of others:

I. Rimbach and Ley[11] measured the hydrogen-ion concentration of boric acid with different quantities of mannitol. From these data the following values were calculated by the methods described in Rec., **49**, 712 (1930). Boric acid = 0.1 mol.

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[10] Kolthoff: Rec. Trav. chim., **45**, 501 (1925).

[11] Z. physik. Chem., **100**, 393.

Boric acid: polyol	pH	ΔpH	n
1 : 6	3.08		
		0.78	2.0
1 : 1	3.86		
		0.75	2.1
1 : 5	3.11		
1 : 4	3.27		
		0.59	2.0
1 : 1	3.86		
		0.46	1.9
1 : 3	3.40		

Boric acid = 0.25 mol.

Boric acid: polyol	pH	ΔpH	n
1 : 2	2.93		
		0.49	2.0
1 : 6	2.44		
		0.74	1.9
1 : 1	3.18		

There is, therefore, no doubt but n is = 2 for these solutions but on the other hand it is easy to understand that for more concentrated solutions, where, moreover tetraboric acid appears, also the remaining OH-groups of the mannitol play a part through which the difficulties that arose in the separation of these acids, find a natural explanation.[12]

II. Years ago van Liempt (Rec., **39**, 358) titrated boric acid diol solutions potentiometrically with alkali. One of his measurements (on fructose) can be used for the calculation mentioned in Rec., **49**, 711 on account of the proportion boric acid : diol = 1 : 5.

In view of the irregular intervals of the pH his measurements appeared to be not very accurate, among other things for the reason that he made use of a very concentrated boric acid and fructose solution, which he greatly diluted with sodium hydroxide during the titration. According to Rec., **49**, 714.

$$K_3 = \frac{[H^+] \times [BD_2^-]}{[HB] \times [D]^2}$$

hence if the initial concentration of boric acid = a, and of the fructose = 5a, and if xa mol of alkalies have been added, then:

$$K_3 = [H^+] \times \frac{xa}{(a - xa)\,(5a - 2xa)^2}$$

The final point of the titration being reached at 15 cc, x is = y/15 if y is = the number of added cc's of NaOH, hence:

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[12] Hermans: Z. anorg. allgem. Chem., **142**, 111 (1925); Fox and Gauge: J. Chem. Soc., **99**, 1075 (1911).

$$[H^+] \times \frac{y}{(15 - y)(75 - 2y)^2} = \frac{a^2K_3}{225} = \text{constant} = c.$$

For the middle part of van Liempt's titration curve, where the error in (15 – y) and in y is slight, and the electrolyte content not too great, and where also the dilution does not vary too much, the following values were calculated:

cc's NaOH	pH	$c \times 10^8$
5	3·21	7·3
6	3·42	6.3
7	3·56	6.5
8	3·69	6.7
9	3·83	6.8
10	4.09	5·5

Accordingly the K_3 appeared to be constant even under these comparatively unfavourable circumstances.

α-oxy-acids

1. In the first place a small orientating calculation will be given in connection with Rimbach and Ley's measurements[11] on α-oxy-acids. They measured the hydrogen-ion concentrations in oxy-acid solutions of different concentrations with and without boric-acid.

If it is assumed that, just as it has appeared with the poly-alcohols, the mono-complex acid may be neglected with respect to the bi-complex acid in these solutions, the following calculation may be made: Let a be the (H^+)-conc. of n × 0.1 mol. of oxy-acid solution without boric acid, and b the (H^+)-conc. of the same solution, but with 0.1 mol. of boric acid, then, if the variation in the conc. of the undissociated acids is neglected, the following equations hold:

$$K_1 = \frac{(H^+) \times (Z^-)}{(HZ)} = \frac{a^2}{n \times 0.1} = \frac{b \times p}{n \times 0.1}$$

$$K_2 = \frac{(H^+) \times (BZ_2^-)}{(HB) \times (HZ)^2} = \frac{b \times q}{0.1 \times (n \times 0.1)_2}$$

p and q being resp. the (Z^-) and the (BZ_2^-) concentrations of the boric oxy-acid mixture.

Hence:

$$p = \frac{n \times 0.1\ K_1}{b},\ q = \frac{n^2 \times 10^{-3}K_2}{b},\ \text{and } n \times 0.1\ K_1 = a^2$$

$$\text{Now } p + q = b = \frac{a^2}{b} + \frac{n^2 \times 10^{-3}K_2}{b}$$

Hence $\frac{b^2 - a^2}{n^2}$ = c must be constant for different values of n

Lactic acid.

Conc. oxy. acid	H^+ conc. without boric acid	H^+ conc. with 0.1 mol of boric acid	$c \times 10^4$
0.1	6.07×10^{-3}	8.36×10^{-3}	0.33
0.2	9.06	17.1	0.52
0.3	11.5	21.7	0.37
0.4	13.5	27.6	0.36
0.5	14.6	35.1	0.40
0.6	15.8	38.0	0.33
0.7	17.1	41.2	0.29

For the mono- and the tri-complex acid, the values of resp. $\frac{b^2 - a^2}{n}$ and $\frac{b^2 - a^2}{n^3}$ would have to be constant, which is, of course not the case in the above observations, where n varies from 1-7.

A similar result, though not so beautiful, is also yielded by the glycollic acid measured by Rimbach and Ley.

II. For the determination of the dissociation constants of the acid complexes of boric acid and α-oxy acids, the pH-curve was determined for the titration of 10 cc 0.1 mol. of oxy acid with 1.0 cc 1.0 mol. KBO_2-solution. Assuming the 1-2 complex acid to constitute the last stage of the tendency to complexity of boric acid, we have, therefore, here four acids side by side, with the following dissociation constants:

$$K_2 = \frac{[H^+] \times [BZ_2^-]}{[HB] \times [HZ]^2} \qquad K_1 = \frac{[H^+] \times [BZ^-]}{[HB] \times [HZ]}$$

$$K_3 = \frac{[H^+] \times [Z^-]}{[HZ]} \qquad K_4 = \frac{[H^+] \times [B^-]}{[HB]}$$

Further, when b mol. of KBO_2 are added:

initial conc. of oxy acid $a = 2[BZ_2^-] + [BZ^-] + [Z^-] + [HZ]$.

all the negative ions $b + [H^+] = [BZ_2^-] + [BZ^-] + [Z^-] + [B^-]$.

all the boric acid $b = [BZ_2^-] + [BZ^-] + [HB] + [B^-]$.

The whole titration curve lying in an acid region, we may neglect the (B^-) conc. with respect to (HB), so that remains:

$$K_2 \times [HZ]^2 \times [HB] = [H^+] \times [BZ_2^-]$$

$$K_1 \times [HZ] \times [HB] = [H^+] \times [BZ^-]$$

$$K_3 \times [HZ] = [H^+] \times [Z^-]$$

$$a = 2[BZ_2^-] + [BZ^-] + [Z^-] + [HZ]$$

$$b + [H^+] = [BZ_2^-] + [BZ^-] + [Z^-]$$

$$b = [BZ_2^-] + [BZ^-] + [HB]$$

For a pretty well equal electrolyte concentration, K_3 may be measured by means of a simple potentiometric titration of the oxy-acid with alkali, so for a definite point of the titration curve K_3, a, b, (H^+) are known; unknown are: K_2, K_1, (BZ_2^-), (BZ^-), (Z^-), (HZ), and (HB).

Hence there are 6 equations, and 7 unknowns.

By the application of a neglection, K_2 can be calculated for a portion of the titration curve, in consequence of which 6 equations and 6 unknowns remain for the general case.

After elimination of the unknown quantities, two equations remain in the end from which the (HZ) cannot be eliminated any more

$$2)\ldots K_2K_3[HZ]^3 - K_2[H^+]^2[HZ]^2 + [H^+]^2[HZ] - [H^+]^2\{a - b - [H^+]\} = 0$$

The value of (HZ) to be approximated from this is filled in, in the following equation, from which K_1 can be calculated

$$3)\ldots K_1 = \frac{[H^+]}{[HZ]} \times \frac{[H^+]\{2b - a + 2[H^+] + [HZ]\} - K_3[HZ]}{K_3[HZ] - [H^+]^2}$$

We now proceed to the computation of K_2:
By division of K_2 by K_1, follows, compare: 1)

$$\frac{[BZ_2^-]}{[BZ^-]} = \frac{K_2}{K_1} \times [HZ]$$

If K_2/K_1 has a value of $\pm 10^3$ or $> 10^3$, as has appeared to be true for the polyols, and as afterwards will appear to be true here too, (BZ^-) may be neglected with respect to (BZ_2^-) over the portion of the titration curve where $(HZ) > 0.02$ mol. as the quantity of (BZ^-) is then less than 5% of the quantity of (BZ_2^-).

These values may be neglected over the part of the titration curve from 0.10-0.40 cc KBO_2.

Hence we get for the calculation of K_2:

$$K_2 \times [HB] \times [HZ]^2 = [H^+] \times [BZ_2^-]$$
$$K_3 \times [HZ] = [H^+] \times [Z^-]$$
$$a = [HZ] + [Z^-] + 2[BZ_2^-] \text{ (initial conc. of the oxy-acid)}$$
$$b = [HB] + [BZ_2^-] \text{ (total boric acid)}$$
$$b + [H^+] = [Z^-] + [BZ_2^-] \text{ (all negative ions)}$$

From these 5 equations (BZ_2^-) (Z^-), (HB), (HZ) may be eliminated after which we get:

$$4)\ldots K_2 = \frac{\{K_3 + [H^+]\}\{b + [H^+]\} - K_3a}{K_3(a - 2b) - [H^+]\{K_3 + [H^+]\}} \times \frac{\{[H^+] - K_3\}^2}{[H^+]\{a - 2b - 2[H^+]\}^2}$$

Recapitulating: with formula 4) K_2 can be calculated over the first part of the titration curve (0.10-0.40 cc KBO_2), with formulae 2) and 3) K_1 can be calculated over the remaining part, where the appearance of BZ^- ions is very perceptible. The pH-curves are measured for α-oxy-iso-butyric acid, cyclo-pentane-α-oxy-carbonic acid, cyclo-hexane-α-oxy-carbonic acid.

Determination of K_3 at an electrolyte concentration varying between 0.025-0.075 mol. by potentiometric titration of 10 cc 0.1 mol. of oxy-acid with 1.0 cc 1.0 N. potassium hydroxide.

	cc's KOH	pH	K_3
α-oxy-iso-butyric acid	0.254	3.387	1.4×10^{-4}
	0.525	3.894	1.4
	0.790	4.438	1.4
cyclo-pentane-α oxy-carbonic-acid	0.267	3.562	1.0×10^{-4}
	0.532	4.066	1.0
	0.792	4.581	1.0
cyclo-hexane-α-oxy-carbonic-acid	0.226	3.514	0.90×10^{-4}
	0.537	4.104	0.91
	0.690	4.383	0.92

Now follow the different points of the determined pH curves for the titration of oxy-acid with KBO_2 with the values calculated for K_2 and K_1.

A typical phenomenon, which has not yet been accounted for, was that the adjustments over the second parts of the titration curves required a good deal of time.

α-oxy-iso-butyric acid

cc's KBO_2	pH	K_2	K_1
0.147	2.664	2.3	
0.194	2.758	2.3	
0.240	2.869	2.2	
0.288	2.991	2.2	
0.336	3.119	2.4	
0.384	3.282	2.4	
0.532	3.934		3.1×10^{-3}
0.582	4.225		3.1
0.630	4.502		3.3
0.731	5.038		3.2
0.783	5.290		3.3
0.836	5.523		3.6

cyclo-pentane-α-oxy carbonic acid

cc's KBO_2	pH	K_2	K_1
0.100	2.641	3.2	
0.144	2.724	2.7	
0.192	2.812	2.8	
0.239	2.901	3.3	
0.285	3.032	3.2	
0.331	3.154	3.2	
0.337	3.312	3.2	
0.616	4.644		3.8 × 10^{-3}
0.663	4.943		3.6
0.712	5.199		3.4
0.762	5.434		3.9
0.808	5.659		3.7
0.854	5.842		4.2

cyclohexane-α-oxy-carbonic acid

cc's KBO_2	pH	K_2	K_1
0.150	2.713	3.9	
0.197	2.795	4.0	
0.246	2.895	4.1	
0.293	3.018	4.0	
0.343	3.166	4.3	
0.390	3.349	3.7	
0.530	4.178		2.3 × 10^{-3}
0.577	4.596		1.9
0.626	4.962		2.1
0.675	5.291		2.2
0.725	5.544		2.3
0.776	5.807		2.4
0.825	6.045		2.4

The result is that it appears from the fact that K_2 and K_1 have been found to be constant for these 3 α.oxy acids, that the suppositions on which formulae 2), 3) and 4) are based, are correct.

In consequence of the fact that K_1, K_2 and K_3 are known, it should now be possible to calculate the quantities of different components accurately for every point of the titration curve, but this cannot be done exactly as K_1, K_2 and K_3 are no pure ionisation-constants, but ion-activity-constants, constants measured in a solution with a considerable electrolyte content.

In order to obtain a good idea of the concentrations of the different components during the titration, these have been calculated for an imaginary acid with $K_1 = 3 \times 10^{-3}$, $K_2 = 3$, $K_3 = 10^{-4}$, and represented in a graph.

It appears clearly that with the ratio alkali: boric acid: oxy acid = 1 : 1 : 2 (A) the BZ_2-ions, and that on the contrary with alkali: boric acid: oxy acid = 1 : 1 : 1 (B) the BZ^- and the Z^- -ions play the most important part.

It is evident that with different concentrations, and especially with other acids with other constants, the graphs will present an entirely different aspect.

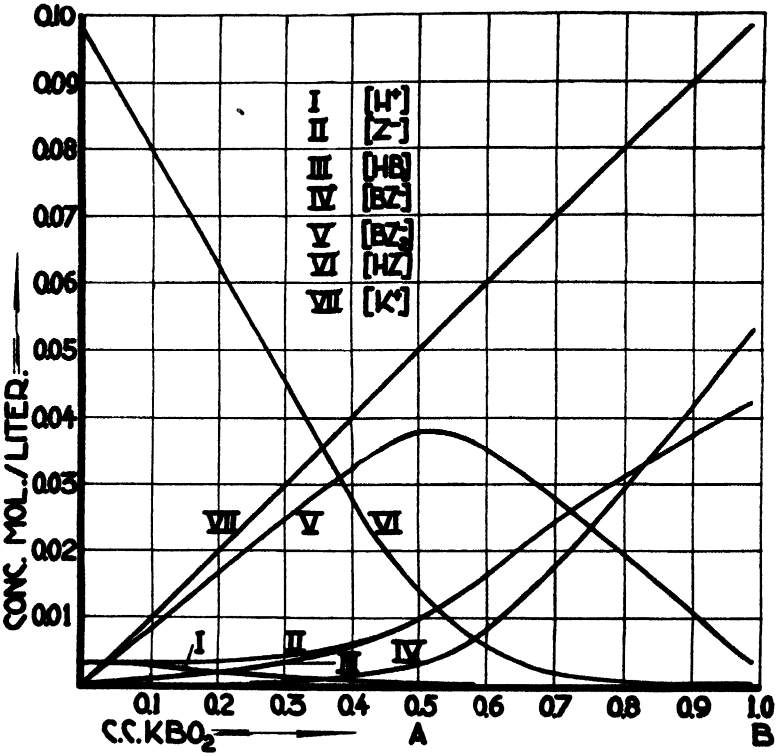


Fig. 1

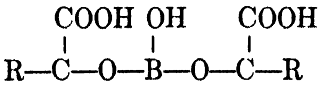
Conclusions

1. The measurements and computations mentioned in Rec. **49,** 711 and in this article have established that the greatest number of molecules of favourable diol or α-oxy acid that one molecule of boric acid in 0.1 mol solution can bind, is *two* for the cases investigated.

2. In three α-oxy acids the presence of the acid consisting of 1 mol. of boric acid and 1 mol. of oxy acid was shown. Also for polyalcohols (fructose, mannitol) the presence of the acid consisting of 1 mol. of boric acid and 1 mol. of diol is found. These investigations will be published later on.

3. The appearance of the two complex acids depends on the dissociation constants K_2 and K_1, and also on the concentration of the free oxy acid.

4. The ring structure proposed by Böeseken, which had already been convincingly proved by the separation of the optically active isomers of boric acid-α-oxy acid compounds,[13,2,3,4,5] has been fully confirmed also by these measurements. How could acids as Bancroft and Davis[1] propose



$$\mathrm{R{-}\overset{\displaystyle COOH}{\overset{|}{C}}{-}O{-}\overset{\displaystyle OH}{\overset{|}{B}}{-}O{-}\overset{\displaystyle COOH}{\overset{|}{C}}{-}R}$$

be monobasic?

5. The existence of such feebly acid complex compounds is plausible for all other (not α-hydroxy-or orthohydroxy) acids.[9]

6. The appearance of tetraboric acid in concentrated solutions[10] and the fact that mannitol possesses still another set of favourable OH-groups, render a study of the concentrated boric acid-mannitol solutions very difficult, which quite accounts for the absence of an "indication of a solid compound in the phase study of aqueous solutions of mannitol and boric acid."

7. It has been explained why Meulenhoff and others, working with solutions in which alkali: boric acid: oxy acid = 1 : 1 : 2, separated the di-complexes[14], whereas Kolthoff[15] demonstrated the presence of the mono-complex in his measurements of the solubility of silver salicylate in boric acid, in which he worked with alkali: boric acid = 1 : 1, the possibility exists, however, that in salicylic acid the ratio K_2/K_1 is entirely different from that in the saturate α-oxy acids examined.

8. The above results leave no room for the assumption that "these phenomena are solubility phenomena," but prove on the contrary that "the increased acidity must be due to the formation of compounds."

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[13] Böeseken: Proc. Akad. Wet. Amsterdam, **27**, 174.

[14] Meulenhoff: Doctor thesis, Delft, p. 61 (1924).

[15] Rec. Trav. chim., **45**, 607 (1925).

A REFRACTOMETER FOR REACTIVE LIQUIDS

BY WALTER CULE DAVIES AND WILLIAM J. JONES

The determination of the refractive indices of some liquids is rendered difficult by their reactive and corrosive nature. For instance, certain organometallic compounds are so quickly decomposed by oxidation on exposure to the air, and most acid halides are so rapidly hydrolysed by the atmospheric moisture, that the measurement of their indices by means of ordinary refractometers, such as the Abbe and the Pulfrich, in which contact with the air is involved, is out of the question. Even if special, air-tight, cells are used with such instruments, troubles are encountered where such liquids as the chlorides of phosphorus and arsenic are placed in contact with the optical glass, which they and their products of decomposition rapidly pit and corrode. For these reasons, where reactive liquids have to be dealt with, a refractometer with an air-tight cell of readily replaceable optical parts is desirable, and such an instrument, based on the principle of the spectrometer with liquid-filled prism, is illustrated in Fig. 1.

The prism, P, is of glass, through which a cylindrical hollow has been bored parallel to the base. The hollow is closed by a thin plane glass front and a back, plane, glass covered, mirror. These parts are kept in position by means of rubber bands, or in certain cases it may be preferable to cement the plates to the prism with Canada balsam. Communication to the hollow is afforded by two tubes carrying taps which are ground into the base and top of the prism, respectively. The assembled empty prism is placed on the prism table, where it is filled, and is held in position by means of the spring clip, C.

The angle of the prism and parts is determined by the use of a standard liquid. This determination was found to be necessary; although the prism used in the present work had itself been accurately cut to 30°, owing to adjustments of the plates, involving the use of bands or of Canada balsam, the composite prism did not actually function with exactly that angle. The standard benzene used for this purpose had the following refractive indices: $n_F^{20°}$ 1.51171, $n_D^{20°}$ 1.49989, $n_C^{20°}$ 1.49527. To take the readings, the source is placed so that the light falls on the rhomb on the left-hand side of the eyepiece. The zero position, in which the ray is reflected back from the front plate along its original path, is obtained by narrowing the slit, controlled by the milled head, S, and bringing the image of the slit into coincidence with the intersection of the cross-wires. The prism with its table is then rotated by means of the arm, A, until the refracted image of the slit is brought into coincidence with the intersection of the cross wires. The refractive index is given by the ratio of the sine of the angle of rotation to that of the angle of the prism, and, the value of the index being known for the standard liquid, benzene, the angle of

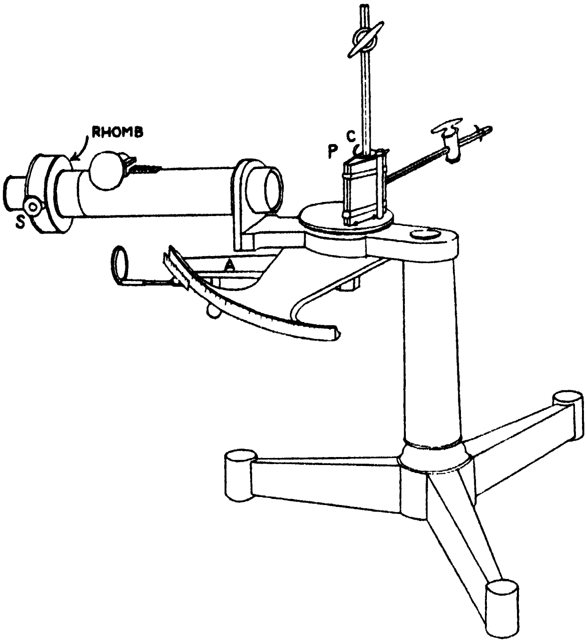
RHOMB
S
C
P
A

FIG. 1

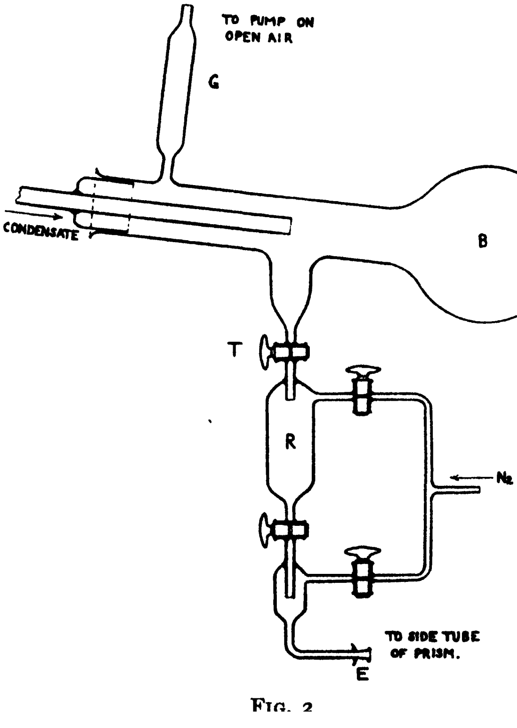
TO PUMP ON
OPEN AIR
G
CONDENSATE
B
T
R
N₂
TO SIDE TUBE
OF PRISM.
E

FIG. 2

the prism and parts is found. For instance, the angle of the prism and parts thus determined in one of the present settings was 30° 2′. The benzene is then removed, without disturbing the plates, from the prism, which is thoroughly dried by a rapid stream of air.

The liquid under investigation, already purified, is now distilled in an all-glass apparatus, and is condensed and collected in the two-way receiver, shown in Fig. 2, with guard tube, G. Air is swept out of the apparatus by the admission of an indifferent gas, and, if necessary, the apparatus is then evacuated. Half of the liquid is collected in the bulb receiver, B, and then the receiver, R, originally horizontal, is turned into the vertical position shown in the figure, and the collection of a specimen is effected in R. The tap, T, is then closed, and the receiver, R, is attached by its ground end, E, to the corresponding ground end of the horizontal tube of the prism, which is now swept out with the inert gas, a guard tube having been affixed to the vertical tube on the top of the prism. The liquid is now allowed to flow into the prism. It is an easy matter to maintain the temperature at the standard, *viz.*, 20°C. As an example we may quote the following measurements of the refractive index of acetyl chloride: $n_F^{20°}$ 1.39335, $n_D^{20°}$ 1.38708, $n_C^{20°}$ 1.38548.

Investigation of the refractivities of highly reactive liquids such as acid chlorides by means of this instrument is now in progress.

In conclusion we have to thank Messrs. Bellingham and Stanley, London, for their help and advice in the construction of the instrument.

Tatem Laboratories,
University College,
Cardiff.
October 28, 1930.

THE THERMAL DECOMPOSITION OF DIAZOMETHANE

BY E. W. R. STEACIE

According to v. Pechmann[1] diazomethane decomposes thermally to give ethylene and nitrogen as indicated by the equation

$$CH_2N_2 = N_2 + \tfrac{1}{2}\, C_2H_4;$$

and if the vapour is heated above 200°C it may explode violently.

Staudinger and Kupfer,[2] however, claim to have used the vapour of diazomethane at 400-500°C in the synthesis of ketene.

An attempt was made by the writer to investigate the slow decomposition of the substance at temperatures below that at which it explodes. This attempt was abandoned after a number of serious explosions, but a few of the results which were obtained may be of interest and are given in the present communication.

Preparation of Diazomethane

Diazomethane was prepared by treating an amyl ether solution of nitroso methyl urethane with a 70 per cent aqueous solution of potassium hydroxide, and refluxing the mixture.[3] The gas evolved was condensed in a bulb immersed in a carbon dioxide-acetone mixture. The liquid thus obtained was fractionally distilled and was stored as a liquid in a bulb at −80°C.

The Products of the Thermal Decomposition

Experiments on the thermal decomposition were carried out by letting small quantities of the vapour into a bulb contained in an electric furnace at temperatures from 140° to 220°C. The progress of the decomposition was followed by pressure measurements made with a McLeod gauge.

In the slow decomposition the products were ethylene and nitrogen as indicated by the equation

$$CH_2N_2 = N_2 + \tfrac{1}{2}\, C_2H_4.$$

This would correspond to an increase in pressure of 50 per cent when the reaction reached completion. Some of the observed increases in pressure under various conditions of temperature and initial pressure were 50, 54, 51, 48, and 54 per cent. The products of the reaction were analysed in a number of cases, and two typical analyses follow.

217°C. Initial pressure 5.2 cms.

$N_2 = 68.8\%$, $C_2H_4 = 28.8\%$

saturated hydrocarbons (as CH_4) $= 2.4\%$.

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[1] Ber., **31**, 2643 (1898).

[2] Ber., **45**, 508 (1912).

[3] v. Pechmann: Ber., **28**, 855 (1895).

187°C. Initial pressure 10.9 cms.

N_2 = 67.2%, C_2H_4 = 32.0%, CH_4 = 0.8%.

These are in satisfactory agreement with the calculated composition from the above equation, viz. N_2 = 66.6%, C_2H_4 = 33.3%.

In the explosive decomposition a large amount of carbon and tarry material was deposited, the gaseous products being mainly nitrogen, together with various hydrocarbons and some hydrogen. This is to be expected since, at the high temperature of the explosion wave, ethylene would be largely decomposed.[1]

The Explosive Decomposition

The explosion limits of the reaction were determined approximately. At 217°C an explosion occurred if the pressure of the diazomethane was above 10 cms. At 187°C the limiting pressure was about 18 cms. Any accurate determination of these limits was impossible since, as will be discussed later, the explosive nature of the substance is very susceptible to traces of organic matter. The explosion limit was definitely lowered, however, by the presence of an inert gas as is usual with an explosion of the chain type. Thus a mixture having partial pressures of 8 cms. of diazomethane and 30 cms. of nitrogen exploded violently at 187°C.

It was found that explosions also occurred at low temperatures due to traces of organic matter such as carbon or tarry material deposited in a previous explosion. In one case a bulb containing about one gram of liquid diazomethane was connected to a small evacuated bulb which was at room temperature. When the pressure of the vapour in the small bulb reached about 5 m.m. an explosion occurred which detonated the supply of liquid at −80°C. A number of serious explosions occurred in this way and, as it was not found possible to control the behaviour of the substance even at −80°C, the work was abandoned.

The Slow Decomposition

Only a few experiments were performed on the slow decomposition. The results of these are listed below:

Slow Decomposition in Quartz Bulb

Temperature °C.	Initial Pressure, mms.	Time in seconds for a 10% increase in pressure, i.e. for 20% completion.
217	52	11
217	45	12
187	109	120
187	54	231
162	155	358
162	87	760
162	45	1435
135	202	9400
135	91	20600
135	45	38000

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[1] Hurd: "Pyrolysis of Carbon Compounds," 56 (1929).

The reaction is apparently bimolecular since the time required for a given fraction of the reactant to decompose is approximately proportional to the reciprocal of the initial concentration.

The addition of powdered quartz to the reaction vessel had no appreciable effect on the rate of decomposition. The reaction therefore is homogeneous.

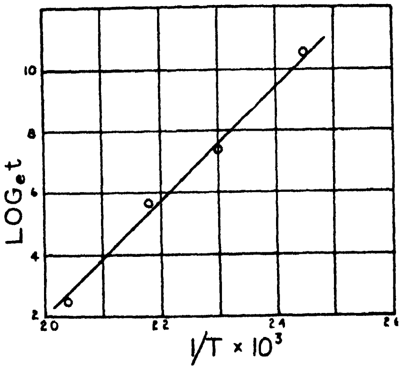

FIG 1

The Temperature Coefficient

In Fig. 1 the logarithm of the time to 20% completion is plotted against the reciprocal of the absolute temperature, for an initial pressure of 45 mm. The points fall satisfactorily on a straight line as required by the Arrhenius equation. The heat of activation calculated from the slope of the line is 36000 calories per gram molecule.

It should be emphasized that owing to the small number of experiments reported these results are to be regarded as merely semi-quantitative.

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A NOTE ON SOME PROPERTIES OF BENZALDEHYDE

BY JAMES R. POUND

It is of course well known that benzaldehyde oxidises rapidly in the air and that finally crystals of benzoic acid separate. Many conditions of this action have been studied recently,—see, for example, abstracts of papers by O. M. Reiff and by M. Brunner (1927); and we have also observed that oxidation occurs chiefly at the free surface of the liquid and on the surface of the containing vessel above the liquid, and also that solutions containing appreciable benzoic acid oxidise less readily than the pure benzaldehyde. We have determined some properties of benzaldehyde and simultaneously the benzoic acid content of the samples.

Commercial benzaldehyde was dried over calcium chloride, with which it possibly forms an unstable compound, and was then distilled in a stream of carbon dioxide; the B. P. (corr.) was 179°-181°; and the product contained some benzoic acid. Some of the distillate was washed with bicarbonate of soda solution, dried over calcium chloride, and filtered off through a filter-plate. Some of the solutions with benzoic acid were made up synthetically and others obtained by oxidation from the original benzaldehyde. The percentage of benzoic acid was determined by titration by carbonate-free caustic soda, using phenol-phthalein as indicator, in alcoholic or aqueous solution. The densities and viscosities at 30° and the refractive index at 20° were found in the usual manner. Typical results are given in the table in C.G.S units.

The density-concentration curve is linear and indicates that $D^{30^\circ}_{4^\circ}$ for the pure benzaldehyde is 1.0365. The densities of solutions containing x% weight of benzoic acid are,—

$$D^{30^\circ}_{4^\circ} = 1.0365 + 0.00125.x,$$

$$\text{and } D^{14^\circ}_{4^\circ} = 1.0567 + 0.00113.x$$

The viscosity-concentration is slightly convex to the concentration-axis and indicates that η^{30° for the pure benzaldehyde is 0.01296.

The refractive index of benzaldehyde varies little as benzoic acid is dissolved in it; probably $\eta^{20^\circ}_{D}$ for pure benzaldehyde is 1.5460, decreases linearly with increasing concentration of benzoic acid, and the $\eta^{20^\circ}_{D}$ for the solution containing 14% acid is 1.5456; however our refractometer only gives n within ±0.0001.

At 7° the solution of benzaldehyde saturated with benzoic acid contains 12.85% acid, and at 13° such contains 14.0% acid.

TABLE I

Properties of Solutions of Benzoic Acid in Benzaldehyde

%wt. Benzoic acid	$D^{30°}_{4°}$	$\eta^{30°}$	$n^{20°}_{D}$
0.23*	1.0371	.01309	1.5460
5.80*	1.04375	.01449	—
1.10	1.0379	.01316	1.5457
8.60	1.0470	.01512	—
13.0	1.0528	.01642	1.5459
14.01	1.05385	.01674	—

Note * These samples were from benzaldehyde after $NaHCO_3$ treatment.

The School of Mines.
Ballarat, Australia.

NEW BOOKS

Diatomaceous Earth. *By Robert Calvert. 23 × 16 cm; pp. 251. New York: Chemical Catalog Company, 1930. Price: $5.00.* In the preface, p. 9, the author says: "The present uses as well as the future possibilities of diatomaceous earth are attributable to its unique properties. Diatomaceous earth consists of the fossil remains of an order of unicellular plants called *Diatomaceae.* The individual particles of the earth are so small that forty million of a given species may be contained in one cubic inch. Yet the microscope shows each one of the millions to be delicately fashioned into a highly ornate structure, with numerous channels, perforations, and nodules, all combining to give an extensive surface area. The composition is nearly pure silica and, consequently, is infusible at a red heat."

The subject is presented under the headings: introduction; present status of the industry; occurrence of diatomaceous earth; mining and preparation of diatomaceous earth for the market; physical properties of diatomaceous earth; filtration medium of diatomaceous earth; filtration of sugar solutions; miscellaneous filtrations with diatomaceous earth; diatomaceous earth in the petroleum industry; action of alkalies upon the diatomaceous earth; diatomaceous earth as an admix in Portland cement and plaster; diatomaceous brick; miscellaneous insulating compositions containing diatomaceous earth; thermal conductance and loss of heat through furnace walls; diatomaceous earth as absorbent; miscellaneous uses of diatomaceous earth.

Fullers' earth must be distinguished from diatomaceous earth, p. 15. "The two earths are different in origin, composition, density, uses, and properties. Yet they are often confused in the general thought. Fullers' earth is of mineral, diatomaceous earth, of vegetable origin. Fullers' earth is a clayey substance, diatomaceous earth nearly pure silica. The one has an unctuous, greasy feel, the other is chalky. In compact form, fullers' earth weighs more than 100 pounds to the cubic foot, diatomaceous earth, 15 to 40. Fullers' earth has sufficient adsorptive power to be useful as a decolorant of oils; diatomaceous earth, unless specially treated, has little adsorptive power and functions in filtrations largely mechanically, as a straining agent, to remove insoluble suspended matter."

"Some diatoms live in fresh, some in salt water. Some lie at anchor. Others of the so-called plankton type float freely. Some appear under the microscope as almost naked skeletons while others show a pronounced gelatinous covering. Nearly all varieties are alike in secreting silica and accumulating a droplet of oil. . . . On the decay of the diatoms, the oil and the silica remain. Occasionally the conditions of growth, wind, or current favor the settling of the silica into great deposits that are only slightly contaminated. A similar concentration of diatom oil, either the primary oil or oil formed by decomposition of the vegetable matter of the diatom, is responsible for much of our petroleum. Certainly such vegetable growth is sufficient in quantity to produce enormous pools of oil, by suitable chemical decomposition. Card and Dun describe a deposit of mud no less than four hundred miles long by one hundred and twenty miles broad, found at a depth of between two hundred and four hundred feet, on the flanks of Victoria Land in 70° south latitude. This deposit is composed of diatom ooze, its thickness is unknown. In the Antarctic Regions the sea is often thick with *Diatomaceae* which also tinge it and the ice a dull yellow. Instances are on record of shallow estuarine harbours being choked by their rapid accumulation," p. 18.

"The present importance of diatomaceous earth is due largely to the widespread use of the powder for filtering raw cane sugar solutions and as an addition to concrete and of diatomaceous brick for thermal insulation. These represent the major uses of diatomaceous earth," p. 25.

"Approximately 2000 tons of diatomite are mined annually at Carlin, Nevada, over three-quarters of which are for insulation purposes, as it is claimed that the best grade material will stand an exceptionally high temperature without shrinkage. A good insulation brick is made using magnesium chloride as a binder. It does not make a good cane-sugar filter medium as the diatoms are too small, but the coarsest is used for beet sugar and molasses, also for clarifying dirty oils from crank-cases, etc. It makes an excellent silver polish and is also used in finger-nail polishes and tooth pastes, as well as for fillers, etc," p. 49.

According to Patty and Glover, "the overburden is removed and the thus exposed diatomaceous earth is quarried by hand, stacked outdoors to dry, milled by impact pulverizers, and conveyed by blowers through a pipe line over a series of hoppers into which the powder settles according to the size of the particle. The very fine dust which does not settle, even in the last hopper, is separated from the air stream by filtration through cloth in a so-called "bag-house." The powders thus obtained are packed in burlap sacks and sold according to grade. . . The product which settles in the single dust chamber or in any of the four hoppers is of satisfactory grade for the regular grade for the regular commercial uses. The fine dust which separates in the cyclone or in the cloth bags is exceedingly fine, free from grit, and much desired by the manufacturers of various polishes, particularly those for lacquered automobiles," pp. 69, 81.

"An excellent absorbent, diatomite is a poor adsorbent. It does not adsorb vapors or gases readily. Neither does it decolorize, to an important degree, liquids filtered through it. That it does adsorb in certain instances is true. For example, an alkaline, alcoholic solution of phenolphthalein, if poured into diatomaceous earth, loses its bright pink color at once and becomes colorless. Also, powdered diatomaceous earth in filtering raw sugar probably retains much colloidal matter and raises the purity of the raw sugar," p. 93.

"Finally, a removal of bacteria and enzymes is sometimes effected by filtration through powdered diatomaceous earth. Brewers of "near-beer" arrest the fermentation, when the alcoholic content approaches that allowed by law, by adding diatomaceous earth to the brew and filtering. Calvert and Knight have found that sugar syrups filtered through diatomaceous earth and then kept in fermentation tubes do not develop gas as quickly as unfiltered syrup. Owen, in very careful tests, has found such filtration removes 99 per cent of the bacteria," p. 100.

"Originally, varnish was 'cleared' by the simple process of settling out the undissolved gums and other solids. Centrifuging was more convenient but did not accomplish an absolute, positive clarification of the varnish. Some of the suspended gums and other solids are so finely divided and so light in weight as to defy every attempt at removal by centrifugal force. Therefore, it was but natural that filtration with pressure filters should persist for the clarification of the higher grades of goods, especially in the larger companies with reputations for the appearance and durability of their product. The absolute certainty of clear goods from the filter-press offsets, in a large measure, the objections accompanying the added labor, floor space, and handling of 'excess varnish.' At the same time, it was recognized that these objections are serious ones, and in many of the smaller varnish factories centrifuges were adopted and were accepted as an answer to the whole problem of clearing varnish.

"Recent developments have changed entirely the position which filter-presses hiterto have held in varnish manufacture. These improvements are, namely, the development for and the application to the varnish industry of the filter-aid Super-Cel which has materially changed the aspect of varnish filtration. Varnish makers are said to be able, through the use of Super-Cel, to accomplish tasks which previously were considered impossible. Ease of filtration, high capacity and more nearly continuous operation of filter-presses are the advantages claimed for the use of Super-Cel, together with greater clarity of product," p. 139.

"Of all the alkalies, lime has perhaps the most interesting effect upon diatomaceous earth. Lime gives a quick change in appearance and a product of interesting though unexplored possibilities. Diatomaceous earth, shaken with water and allowed to stand, settles slowly. With the usual grade of earth, the supernatant liquor will be turbid after even a day of subsidence. But, if lime is added to the suspension and the mixture boiled, coagulation occurs immediately. Now, on even brief settling, the supernatant liquor becomes quite clear. As the boiling is continued for an hour or more, the lime in solution apparently combines with the surface silica of the particles of diatomaceous earth, with attendant enormous swelling.

"The properties of the lime-treated earth are quite different from those of the original earth. A 10-gram sample of diatomaceous earth that settles in distilled water to a volume of 33 cc. has been found, after boiling for three hours with 50 per cent of its weight of lime in aqueous suspension, to occupy a volume of 375 cc. The increase in volume of settled material is over 1,000 per cent. Furthermore, Calvert finds the lime-treated diatomaceous earth to filter water at 4,600 per cent of the rate for the untreated earth. Also, the swollen product after being baked can adsorb vapors of volatile liquids, whereas the original earth has practically no adsorptive capacity.

"The product, when dried at ordinary temperature, is slightly whiter and smoother to the feel than the original diatomaceous earth. Also, the dry lime-treated material weighs only 5 pounds to the cubic foot, as compared to 7 or 8 for the untreated earth packed in the same manner," p. 156.

"Admixture of powdered diatomaceous earth with plaster produces a notable increase in spreading power. Admixture of the earth with Portland cement causes such conspicuous improvements in the quality as to justify the belief that the use in concrete may soon constitute the largest single demand for diatomaceous earth. Already this use is very important," p. 160.

"The firing of diatomaceous brick, in the usual manner, above 1900°F. converts a part of the silica (which comprises more than 90 per cent of the earth) into cristobalite, a highly objectionable, crystalline form. Cristobalite undergoes an abrupt change in volume at certain transition temperatures, as it passes from one crystal form to another. One such change amounts to approximately 1 per cent in length and occurs when the cristobalite undergoes a temperature change of only a few degrees at the critical point. If the cristobalite is cooled through this critical range, the change of 1 per cent in length is one of contraction. If it is warmed, the change is an expansion of a like amount. This, perhaps, explains why insulating bricks that have been improperly made will often spall when only a match flame is applied to the corner of the brick.

"To avoid the formation of cristobalite and consequent spalling, Coss fires his brick in the presence of an agent that favors, it is said, the formation of tridymite instead of cristobalite. Thus, he fires in the kiln to 2500°F. or higher without producing a spalling brick. He seems to obtain a large proportion of the desired tridymite, which, unlike cristobalite, has no transition temperatures at which it undergoes such sudden change of volume as to crack the brick.

"The agent which is used to cause the transformation of amorphous silica of the natural earth into tridymite of this brick is usually 1 to 3 per cent of lime. As a binder, there is used 2 to 7 per cent of a refractory of clay-like composition, such as feldspar. A grog of calcined material, for example, 12 per cent, and a small amount of plastic clay may also be used, p. 185.

"The user of diatomaceous insulation is interested more in the thermal conductivity and the amount of heat that will be saved by the use of the insulation than in the methods of manufacturing it. He is interested, for example, in such results as those obtained from the insulation of 90-ton annealing furnaces in a large malleable iron works. The insulation of walls, arches, and doors with a 4-1/2-inch course of Nonpareil insulating brick decreased the fuel oil consumption, for each ton of product, to 40 gallons as compared to 60 gallons in the older type of uninsulated furnaces. On a total production of 60 tons a day, the fuel saving is 1,200 gallons a day. At 3 cents a gallon this saving amounts to more than $10,000 a year," p. 200.

"The solidifying of alcohol by diatomaceous earth is an interesting illustration of the high degree of porosity of the earth, the amount which may be absorbed being very large. Thus, 100 cc. of the wet paste can be made to contain 86.4 cc. alcohol without being so fluid as to allow leakage of the alcohol from the paste when the container is inverted, either while cold or while the alcohol is burning and the composition is, therefore, warm. To make such a solidified alcohol one mixes, for example, 30 grams of diatomaceous earth, of the quality known as Filter-Cel, with 86.4 cc. alcohol. Although the diatomaceous earth when dry, is very bulky, the actual net volume of the 30 grams of silica composing the skeletons is 30 divided by 2.2 (the approximate specific gravity of such silica) or only 13.6 cc.

"Alcohol thus absorbed in diatomaceous earth is being marketed in Germany, it is said, under the name 'Lithosprit.' In the United States, solidified alcohol or 'canned heat' is now preferably made by allowing a warm solution of soap in alcohol to set to a gel on cooling or by the precipitation of pyroxylin in a dilute alcoholic solution," p. 221.

"Silica *per se* is a poor catalyst as compared with the oxides of iron or aluminum or with many other oxides. Yet the very large extent of surface in diatomaceous earth, its condition of neutrality, insolubility, and inertness under most conditions, its low density, and slow rate of settling from solutions make diatomaceous earth an excellent supporting agent for catalysts," p. 235.

The photomicrographs are good. The reviewer was especially interested in Fig. 2 of diatoms from New Zealand. *Wilder D. Bancroft*

Tables annuelles de constants et données numériques de chimie. (*Annual Tables of Constants and Numerical Data, Chemical, Physical, Biological and Technological*). *Edited by Ch. Marie. Published by the International Committee appointed by the Seventh Congress of Applied Chemistry. Vol. VII, Parts 1* and *2, 1925-1926. 28 × 23 cm; pp. Part 1, xxxv + 946, Part 2, xv + 950. New York: McGraw-Hill Book Company, 1930. Price: $25.00.* The new volumes of tables give a very valuable survey of the numerical data discovered in the years 1925-26. As was the case for the earlier volumes, the tables are divided into more than fifty sections, each written by specialists who are well known in their respective fields. Two new sections have been introduced into Part 2 on Explosives and Explosions in Gaseous Mixtures and two old sections, those on Photography and Geophysics, have been omitted. The specialists in charge of the last two sections prefer that these subjects be dealt with once in every two volumes.

Since there is a large amount of explanatory description given with some of the tables, the various chapters partake somewhat of the nature of monographs. The descriptive matter makes the tables more valuable in that it will not be found so necessary to refer from them to the original literature. When this is necessary, as in the case of details of preparation of new compounds, the reader is aided by being given the number of the page on which the new substance is described.

One feature of the tables which increases their value to the searcher through the literature is the bibliography of papers whose contents cannot readily be expressed in tabular form. It is of interest to note to what extent the attention of the scientific world is being directed to the study of spectra. More than 450 pages are devoted to data on emission and absorption spectra, out of a total of 1896 pages. The chapters on dielectric constants and on X-ray analysis of crystals are also very largely augmented.

The Secretary of the International Committee, Dr. Marie, announces that Volume VIII for the years 1927-28 is already in the press and should appear very shortly. After the publication of this volume, it is proposed to commence a yearly publication of the annual tables. The International Committee is to be congratulated on the manner in which they have overtaken the arrears of publication. *W. E. Garner*

Jahrbuch des Forschungs-Instituts der Allgemeinen Elektrizitäts-Gesellschaft. *Vol. I, 1928-1929. 30 × 22 cm; pp. 240. Berlin: Julius Springer, 1930.* The scope of the research work of the laboratories of those great corporations whose interests depend on applications of pure scientific knowledge is year by year growing wider, and their outlook more philosophic. It *pays*, in every good sense of that much-abused word, to take the long view. And so we find engineering companies fostering research on surface-forces in liquids, and telephone research laboratories enlisting the aid of physicists, physiologists and psychologists. Now we welcome the first volume of the Yearbook of the A. E. G. The range covered by the papers is remarkable, and to attempt to consider it in any detail within the limits of a brief review is an impossible task. Briefly, the volume is made up of some thirty-five papers grouped together under seven headings—Akustik, Elektrotechnik, Elektronenphysik, Atomphysik, Atomchemie, Stoff-physik and Elektro-optik. Subjects so diverse as sound-films, contact potentials, the application of electron-waves to the analysis of crystal structure, the frequency curves of membranes, and the electrical conductivity of molten silicon—to name but one or two titles—are discussed both experimentally and mathematically, and the volume closes, appropriately enough with an essay under the heading "Sollen die technisch-physikalischen Forschungslaboratorien der Industrie rein wissenschaftliche Forschung betreiben?"

The volume is well-produced and bound, and the illustrations, whether line drawings or photographic reproductions, are excellent of their kind. *A. Ferguson*

Solvents. *By Thos. H. Durrans. 22 × 14 cm; pp. xv × 144. New York: D. Van Nostrand Company, 1930. Price: $5.00.* In the preface, p. vii, the author says: "Both the number of organic solvents which are available to industry and the extent to which they are used have increased greatly during the recent years, and there is in consequence a need for a scientific exposition of the technical application of solvents, more particularly in connection with the cellulose-lacquer industry. . . .

"The first part of this book takes the form of a more or less connected series of chapters dealing with the fundamentals in a broad and simple manner. The second part is of a more utilitarian nature and deals comprehensively with individual solvents, mainly with the view of facilitating the intelligent use of these solvents in the cellulose-lacquer industry."

The chapters in the first part are entitled: introduction; solvent action; solvent power; plasticising solvents; solvent balance; viscosity; vapour pressure; imflammability; toxicity. In the second part of the chapters are: introduction; hydrocarbons; alcohols; ketones; esters; glycols; cyclohexane derivatives; chloro-compounds; furfurals; plasticising solvents.

It should be noted that the solutions which the author discusses are practically exclusively colloidal solutions. "It is well known that certain varieties of cellulose nitrate are soluble in a mixture of alcohol and ether, although not soluble in either liquid separately. Neither of these liquids contains any group, such as carbonyl, which usually imparts solvent properties, as, for instance, does acetone or amyl acetate," p. 1.

"If to a solution of cellulose nitrate a miscible non-solvent be gradually added, a dilution is ultimately reached, at which the cellulose nitrate begins to be thrown out of solution either as precipitate or as gel. The solution is said to 'tolerate' the addition of this definite proportion of the diluent under the conditions of temperature and cellulose-nitrate content obtaining. It is common to regard tolerances or dilution ratios as a measure of the solvent power of a solvent," p. 5.

"Plasticisers are solvents which are practically non-volatile; they may be liquids or solids, the latter being known as 'solid-solvents.' The term 'solid-solvent' arose from the use of the solid, camphor, which is a ketone and , like many other ketones, dissolves cellulose nitrate. If a solution of a cellulose ester be allowed to evaporate so as to leave a film, a certain but diminishing quantity of the solvent remains in the film according to the conditions obtaining. This small quantity of solvent imparts to the films a degree of softness or plasticity depending on the solvent and the quantity of it which is present," p. 9.

"The terms 'plasticiser' and 'softener' are not quite happy ones, for what is really desired is not a soft or plastic film but a stable, highly elastic, non-shrinking film with a hard non-scratchable surface. A soft film is one which is susceptible to deformation of its surface; a plastic one retains such deformation; an elastic film returns quickly to its original form," p. 10.

"Platicisiers have a pronounced effect on 'secondary flow,' a loose term applied to the very slow smoothing effect which takes place shortly before the film sets and no longer is capable of flowing. The gloss of a film is largely governed by this secondary flow and it is for this reason that high-boiling solvents tend to produce glossy films, the slow rate at which the solvent evaporates allowing time for microscopic irregularities of the surface to disappear," p. 11.

"For many years it was not possible to make satisfactory factory lacquers with the cellulose nitrates then available, since those nitrates gave solutions of excessively high viscosity when prepared in a state sufficiently concentrated to ensure films of the desired thickness and strength. Many, more or less successful, attempts were made to reduce this viscosity by employing various solvents, but this generally resulted in introducing other undesirable characteristics. It was not until the introduction of the low-viscosity cellulose nitrates, such as the well-known 'half-second cotton,' took place, that the widespread use of such lacquers became possible; even now it is common practice to 'load' the lacquer with resins for the purpose, among others, of giving 'body' to a film without of necessity producing unduly viscous solutions.

"The viscosity of a lacquer may be adjusted in several ways; thus mixtures of different cellulose nitrates may be employed, these being available in grades giving a wide range of viscosity, or the viscosity may be varied by suitable choice of solvent or solvent mixture. Viscosity and vapour pressure are apparently to a considerable extent concomitant properties, the greater the vapour pressure of a solvent the lower the viscosity of its solutions," p. 18.

"The lowering of temperature of a solvent evaporating in free air causes the air in its immediate neighbourhood to fall in temperature, and if the humidity of this air be sufficiently great a temperature below that of the dew-point may be reached and water will be deposited. If the solvent contain a substance insoluble in water, for instance, cellulose nitrate or resin, this deposition of water may cause their precipitation with the consequent formation of a white opaque film on the surface of the solution; this effect is known as 'chilling.' If the solvent is one able to dissolve water to a considerable extent, such as ethyl lactate, diacetone alcohol or ethyl alcohol, this chilling effect may be delayed, since the water may be dispersed in a greater depth of the solution. If, on the other hand, water is completely insoluble in the solvent no chilling can occur, since the water will merely deposit on the surface and not penetrate at all," p. 30.

"It is safe to say that the vapours of all volatile substances are toxic or at least narcotic, if they be inhaled in a sufficiently concentrated state for a sufficient length of time. With some the effect is merely that of suffocation caused by the deprivation of oxygen, others cause anesthesia, whilst a third class includes those definitely poisonous by reason of some physiological action, causing functional derangement of the metabolism. The three classes are not closely defined but merge one into the other and vary with the individual. The majority of lacquer solvents belong to the earlier classes, the term 'solvents' being taken to include the diluents. . . .

"The poisonous effects of most solvents is not cumulative, and their vapours can be inhaled without any apparent effect, provided that they are present in a sufficiently diluted state; prolonged inhalation of such dilute vapours has been known to give immunity to the poisoning by concentrations normally lethal. It has been found, for instance, that workmen constantly employed in the manufacture of ether cannot be anaesthetised in the normal manner by this substance. It should, however, be realised that the continual inhalation of quite small quantities of solvent vapours cannot but have a deleterious effect on the general health, although the effect may not be sufficiently pronounced to be apparent; generally speaking the risk is not greater than that obtaining in other industries, but the importance of adequate ventilation is to be emphasised.

"With some solvents, however, the effect is cumulative, notably with methyl alcohol, tetrachloroethane, tetrachloroethylene and carbon disulphide, although some persons are insensitive to the action of the last-named. Prolonged exposure to benzene vapour has also been found to be highly dangerous, especially to persons of advanced age. Turpentine vapour is poisonous to some, and it would appear that the poisonous action of lead-pigmented paints may have been wrongly ascribed in some instances to the lead pigment; 4 to 6 mg. of turpentine per litre of air can produce symptoms of poisoning; 16 mg. per litre killed a cat within one hour.

"Of the various classes of solvents employed, the chloro-compounds are undoubtedly the most poisonous, and they are potent anaesthetics. Carbon tetrachloride and tetrachloroethylene are definitely poisonous, causing enlargement of the liver. This disease, when produced by the action of the latter solvent, is notifiable in England. In Germany, the use of tetrachloroethylene is forbidden. Tetrachloroethane is also said to be highly poisonous, but trichloroethylene is relatively harmless, whilst di-chloroethylene causes dermatitis," p. 40.

"In many cases it is not desirable or expedient that a chemically-pure substance should be used for lacquers. In some instances the presence of 'impurities' considerably enhances the desirable properties of a solvent. On the other hand, the cost of removing certain impurities is out of proportion to the advantages to be gained," p. 45.

The second part contains chiefly data concerning the different substances used as solvents, plasticisers, etc.

Wilder D. Bancroft

Application of Interferometry. *By W. Ewart Williams. 19 × 13 cm; pp. iv. + 104. London: Methuen and Co., Ltd., 1930. Price: 2 shillings, 6 pence.* This small monograph, written for advanced students, contains a clear and correct presentation of the fundamental principles of interferometry. The different methods of obtaining interference effects are divided into such in which the interfering beams start out from a primary line or point light-source or from a similar secondary source, such as a narrow slit ("division of wave-front") and such in which a broad beam is divided by a partially reflecting surface and later is re-united ("division of amplitude") .

For the physical chemist, instruments in the former category are particularly important (the Rayleigh interferometer and the designs worked out by Haber and Löwe are of this type). The methods for size measurement of microscopic and ultramicroscopic objects, worked out by Gehrcke, O. v. Baeyer and Gerhardt, employ the same principle, and are analogous to the method developed by Michelson for the determination of the angular diameter of the stars.

The Jamin and Mach instruments, belonging to the second category are also of interest to the physical chemist, applicable as thev are to the investigation of reaction rates in gaseous systems.

Finally, the various interferometers for the examination of the fine structure of spectral lines (Fabry-Perot; Lummer-Gehrcke) are of importance to the modern spectroscopist.

The manifold possibilities offered by interferometry for purely physical measurements of length and of thickness, form the main theme of the present small volume, and it should be a real stimulus for physical chemists to see set out so clearly the close relations which exist between their own interferometric experiments and the most precise measurements of modern physics.

Fritz Weigert

German for Chemists. *By Louis de Vries. 23 × 16 cm; pp. vi + 178. Easton: The Chemical Publishing Co., 1929. Price: $3.00.* In the preface the author says: "This text contains material taken from the works of well-known Chemists, such as Emil Fischer, Wilhelm Ostwald and others. The different chapters embrace many phases of chemistry, including Organic, Inorganic, Analytical, Biophysical, Physiological and Nutritional, Soil, Plant, and Enzyme Chemistry. The reader, prepared for the use of students who wish to acquire a reading knowledge of German, gives in addition to practice in reading the language, an introduction to German chemical literature."

The selections are well made and the reviewer confesses both to pleasure and profit from reading the book. In the vocabulary verbs with separable prefixes have a hyphen between verb and prefix. That simple little detail will make life a good deal easier for the student.

There are several misprints which should be corrected in future editions: Vergroszerung, p. v; kapilla, p. 17; Gesets, p. 25; Kekule, p. 43 and elsewhere; versichieden, Wurtz, p. 45; umstandilch, p. 66; Herterozyklus, p. 76; nebeneiander, p. 77; Zukkerarten, p. 103; geblidet, p. 104. These are obvious misprints but they might bother the beginner. The author has Inhalt in the vocabulary and Jnhalt in the text, p. 8. The reviewer thinks that Deutsche chemische Gesellschaft, p. v, should not be written with three capitals.

Wilder D. Bancroft

THE HEAT CAPACITY AND FREE ENERGY OF FORMATION OF ETHANE GAS*

BY VICTOR R. THAYER WITH GEBHARD STEGEMAN

A number of thermodynamic calculations have been made by Francis[1] and Smith[2] from which the optimum conditions for certain reactions may be predicted. Both writers admit that some of their results are reduced to the status of estimates, due to inadequate and uncertain specific heat data. This investigation involves the redetermination of the specific heat of ethane gas for reasons which are indicated.

Dixon, Campbell, and Parker[3] measured the velocity of sound in various gases, including ethane, and used the data to evaluate the respective specific heats. Their results for ethane, recalculated by Partington and Shilling[4] are as follows:

Temperature	Cp.
10°C.	11.015
50°C.	11.610
100°C.	12.637

The following direct measurements of Cp for ethane are reported by Scheel and Heuse:[5]

Temperature	Cp.
−82°C.	10.43
−35°C.	11.04
+15°C.	12.40

The divergence between the two sets of data is apparent in Fig. 1. The value of Cp at 15°C., obtained by interpolation of Dixon, Campbell, and Parker's results, is 11.09. The difference between this and the value of 12.40 obtained by Scheel and Heuse, amounts to approximately 11 percent.

Although the results of Dixon and his co-workers at high temperatures have been criticized[6] because his assumptions regarding the effect of the inclosing tube on the velocity of sound are now believed to be incorrect, his

* Contribution No. 203 from the Department of Chemistry, University of Pittsburgh.

[1] A. W. Francis: Ind. Eng. Chem., **20**, 277 (1928).

[2] D. F. Smith: Ind. Eng. Chem., **19**, 801 (1927).

[3] Dixon, Campbell and Parker: Proc. Roy. Soc., **100A**, 1 (1921).

[4] Partington and Shilling: "Specific Heats of Gases," (1924).

[5] K. Scheel, and W. Heuse: Ann. Physik, (4) **37**, 79 (1912); **40**, 473 (1913).

[6] Eastman: J. Am. Chem. Soc., **50**, 727 (1928).

data[7] at room temperature, except in the case of ethane, are in fairly close agreement with those of Scheel and Heuse. The values in the following table indicate this:

Gas	Cp Dixon	Cp Scheel and Heuse	Temp.
C_2H_4	10.33	10.22	18°C.
CO_2	8.84	8.88	20°C.
N_2	6.92	6.98	20°C.

The 11 percent variation in the case of ethane can therefore hardly be attributed to an error of method.

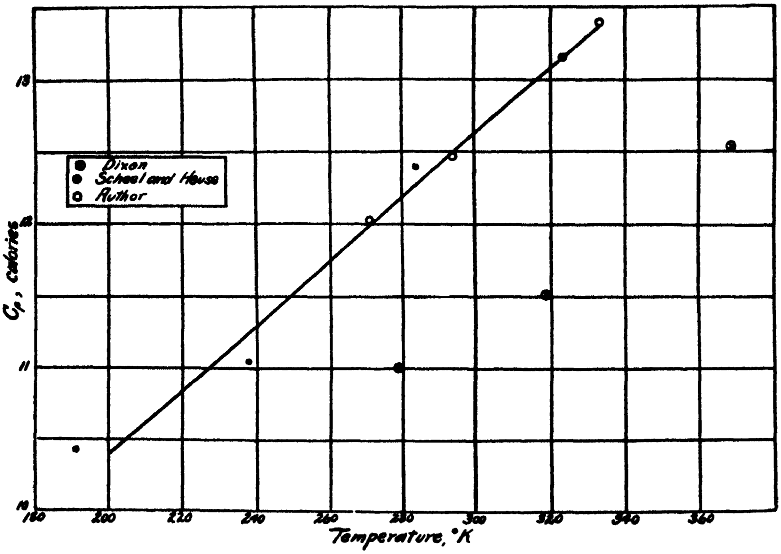

FIG. 1

Preparation of Ethane. Ethane was prepared by the method of Murray[8] modified by suggestions of Loomis and Walters.[9] Briefly, the procedure was as follows: electrolysis of a 60 percent solution of potassium acetate with platinum electrodes, removal of CO from the anode gases by pipettes of the Orsat type, passage of the gas in turn through fuming sulfuric acid, 98 percent sulfuric acid, potassium hydroxide, and phosphorous pentoxide, condensation to a solid; and fractional distillation. Two samples, the second of which received two additional distillations, showed identical specific heats within the limits of experimental error.

Calorimeter. The design of the constant flow calorimeter follows that of Scheel and Heuse.[10] Its detail is shown in Fig. 2 with the path of the gas

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[7] Partington and Shilling: op. cit., 190–199.

[8] Murray: J. Chem. Soc., **61**, 10 (1892).

[9] Loomis and Walters: J. Am. Chem. Soc., **48**, 1052 (1926).

[10] K. Scheel, and W. Heuse: Ann. Physik, (4) **37**, 79 (1912).

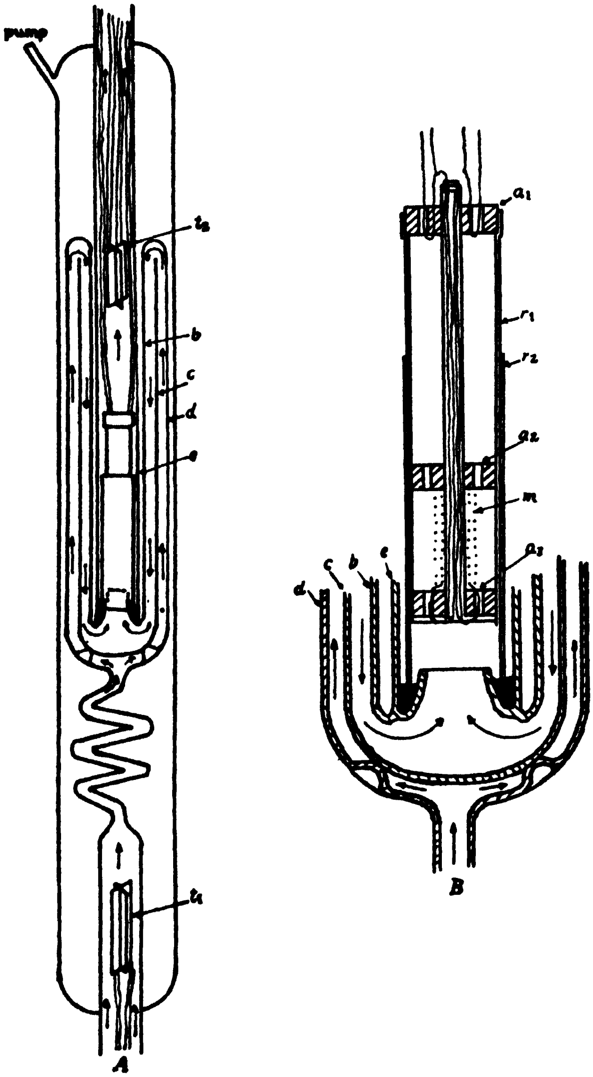

FIG. 2

stream indicated. The relation among the observed specific heat, the true specific heat, and the radiation loss is given by the following equation:

$$Cp = \frac{E}{M\Delta T}\left[1 - \frac{K}{M^2}\right]$$

where

Cp = true specific heat in Watt-seconds per gram,
E = energy input in Watts,
M = grams of gas flowing per second,
ΔT = temperature rise in the gas stream
K = heat loss constant for the calorimeter.

This equation may be considered a straight line in which E/MΔT and E/M$^3\Delta$T are variables, and Cp and K are constants. The constants are evaluated by making a number of observations with different values of M, adjusting E each time so as to keep T approximately constant, and obtaining the equation of the straight line by the method of least squares. The value of K so obtained may then be used to reduce individual observations. The constant for the calorimeter was found to have the same magnitude (0.000046) with either air or ethane.

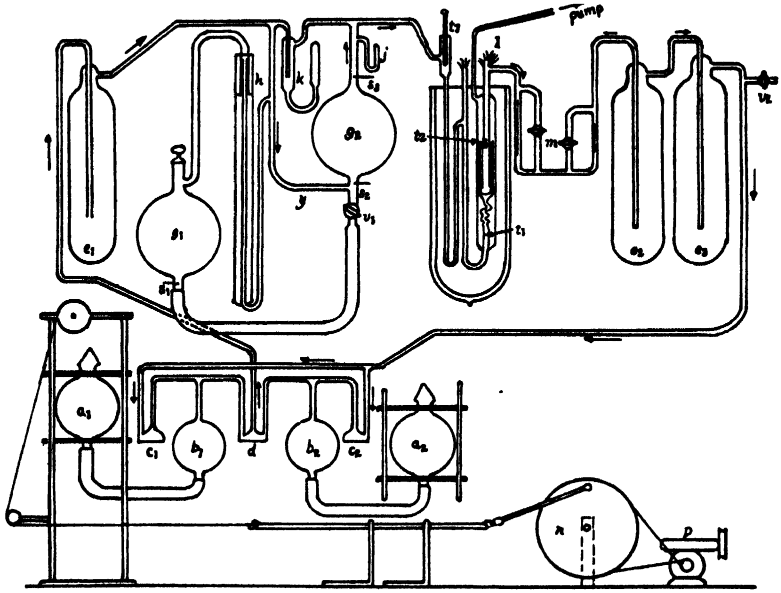

FIG. 3

Platinum resistance thermometers, constructed and calibrated according to specifications of the Bureau of Standards[11] are designated t_1 and t_2 in the detailed drawing of the calorimeter (Fig. 2).

The heating element, shown in detail in Diagram B, Fig. 2, consisted of about 150 centimeters of No. 36 double silk insulated manganin wire wound on a small bore glass tube. A roll of copper gauze was slipped over the coil and inside the brass tube r_1, the whole being held in place by perforated disks a_2 and a_3 of hard rubber. Tube r_1 above disk a_2 was packed with copper gauze and was closed at the top by disk a_1.

The gas circulating system is shown in Fig. 3. The arrangement consists of four units; the circulating pump $a_1a_2b_1b_2c_1c_2d$; the calorimeter 1; the flow meter g_1g_2hkj; flow adjusting devices which are large bulbs $e_1e_2e_3$, used to smooth the flow; and the by-pass capillaries, m, used to vary the resistance.

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[11] H. C. Dickinson, and E. F. Mueller: Bureau of Standards Sci. Paper No. 200.

The direction of flow is indicated. Continuous reciprocation of the bulbs a_1 and a_2 operates the pump.

The flow meter was operated without interrupting the constant passage of the gas stream as follows:

The gas was circulated to the calorimeter by way of the bulb g_2. When it was desired to measure the rate of flow, the valve V_1 was opened, and the bulb g_1 which was full of mercury raised at such a rate that the pressure in the bulb g_2 which was indicated on the manometer j, remained at the usual level. The flow of mercury from g_1 to g_2 blocked the normal path of the gas, which was then diverted to the space being vacated in g_1 by way of the movable seal h.

Timing the flow of mercury between the wires S_1 and S_2 measured the number of seconds normally required for the gas volume contained between the wires, to flow through the calorimeter. The pressure of the gas was measured on the manometer j, and its temperature by the thermometer t_3. Its density and in turn the mass of the gas flowing per second could thus be calculated. When the bulb g_1 was lowered, so that it refilled with mercury, the gas contained in it and also that approaching from the pump was forced out across the by-pass k, a part entering g_2 and the rest proceeding at nearly normal rate to the calorimeter.

As bulb g_1 was emptying of gas, the total resistance to flow in the system was increased slightly, due to the introduction of the by-pass k. The rate of flow was therefore slightly lowered, and the temperature of the gas stream above the heater slightly raised. It was therefore necessary to take a final reading of the temperature increase in the gas stream before flow measurements were begun, or to allow 30 minutes after the latter measurements were completed for equilibrium to be reestablished in the calorimeter.

All the required potential measurements were made with the use of a White Double Potentiometer.

As a test of the reliability of the apparatus and the method, the specific heat of dry carbon dioxide free air was determined at room temperature.

Four of the more recent investigations of the heat capacity of air are listed.

Scheel and Heuse[12]	continuous flow	6.965
Gruneisen and Merkle[13]	velocity of sound	6.936
Hebb[14]	velocity of sound	6.952
Shields[15]	adiabatic expansion	6.947

The value obtained in this investigation as a result of thirteen determinations, at varying rates was 6.495 cals. per mol. Three typical determinations of the thirteen are listed in Table I below.

[12] Scheel and Heuse: Ann. Physik, (4) **37**, 79 (1912).

[13] Gruneisen and Merkle: Ann. Physik, (4) **72**, 193 (1923).

[14] Hebb: Trans. Roy. Soc. Canada, **13**, (3), 101 (1919).

[15] Shields: Phys. Rev., (2) **10**, 525 (1927).

TABLE I

Temp. °C.	M g/sec.	E Watts	ΔT °C.	$\frac{E}{M\Delta T}$	Specific Heat in Watt Seconds per gram
22.40	.02041	0.1009	4.351	1.136	1.011
22.40	.01956	0.0992	4.460	1.138	1.001
22.40	.02668	0.1249	4.324	1.082	1.012

$K = 0.000046$

The condensed results for ethane are listed in Table II.

TABLE II

Temp. °C.	Specific Heat in Watt Seconds per Gram	Specific Heat in Cals. per Mol
2.20	1.675	12.03
24.50	1.736	12.47
54.50	1.833	13.17
64.40	1.865	13.40

Free Energy of Ethane. The free energy of formation of ethane was calculated by the usual formula:

$$\Delta F = \Delta H_0 - \Delta\Gamma_0 T\ln T - 1/2\ \Delta\Gamma_1 T^2 - \ldots\ldots\ldots\ldots\ldots + IT$$

The coefficients of T are defined by the following equations:

$$\text{Heat of Reaction} = \Delta H = \Delta H_0 + \Delta\Gamma_0 T + 1/2\ \Delta\Gamma_1 T^2 + \ldots\ldots\text{etc.}$$

$$\Delta Cp = \Delta\Gamma_0 + \Delta\Gamma_1 T + \ldots\ldots\ldots\ldots\ldots\text{etc.}$$

$$Cp = \Gamma_0 + \Gamma_1 T \quad + \ldots\ldots\ldots\ldots\ldots\text{etc.}$$

ΔCp is obtained by summing the equations for the heat capacities of the substances involved, considering reactants positive and resultants negative.

According to the data of this investigation, the heat capacity of ethane is represented by the equation:

$Cp = 5.981 + 0.2193\ T.$

Francis[1] gives the following values for carbon and hydrogen:

Carbon: $Cp = 1.1 + 0.004\ T,$

Hydrogen: $Cp = 6.65 + 0.0007\ T.$

Also, Francis gives $\Delta H_{298} = -23{,}075.$

Accordingly:

$$\Delta Cp = -16.17 + .012\ T$$

$$\Delta H = \Delta H_0 - 16.17\ T + .006\ T^2$$

$$-23{,}075 = \Delta H_0 - 16.17\ (298) + .006\ (298)^2$$

$$\Delta H_0 = 18{,}789.$$

For ethane, therefore:

$$\Delta F = 18{,}789 + 16.17\ T\ln T - .006T^2 + IT.$$

Smith[2] estimates by the third law of thermodynamics applied to fugacity data that $\Delta F_{298} = -10{,}700$. Using this figure to evaluate I, the equation for the free energy then becomes:

$$\Delta F = -18{,}789 + 16{,}17\ T\ln T - .006T^2 - 63.9T.$$

Francis who used the data of Dixon, Campbell, and Parker (See Fig. 3), gives the following equation for the free energy of ethane:

$$\Delta F = -18{,}789 + 15.18\ T\ln T - .004T^2 - 62.8T$$

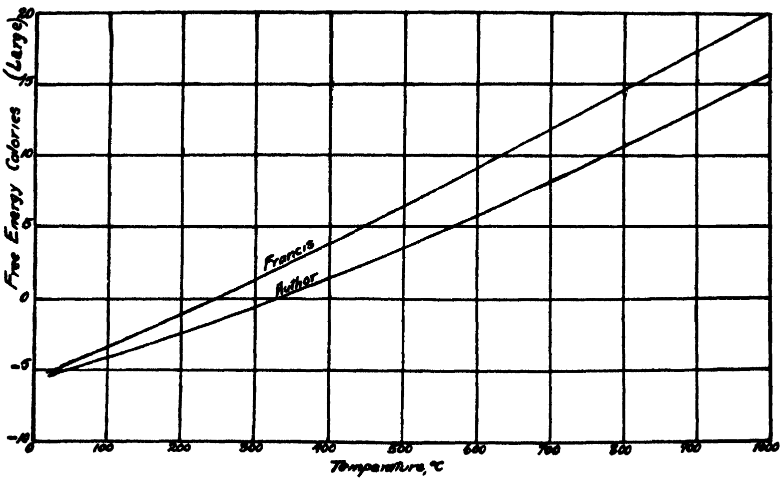

FIG. 4

The latter two equations are represented graphically in Fig. 4.

The precision attained in the measurment of the values reported by the writers was such that the results are believed to be accurate within one percent.

The writers wish to acknowledge the criticism and aid given by Dr. A. G. Loomis and Dr. R. Wiebe of the United States Bureau of Mines, and to express their appreciation to Mr. G. St. J. Perrot, the Director of the Bureau, for the use of facilities which made this investigation possible.

Summary

The heat capacity of ethane gas has been measured at various temperatures and the values obtained, together with those of other investigators are shown graphically in Fig. 1.

The free energy of ethane gas has been recalculated using the specific heat data obtained in this investigation in place of the results of Dixon, Campbell, and Parker, which have been used in previous calculations reported in the literature. The values for the free energy together with those calculated by Francis appear in Fig. 4.

FURTHER STUDIES IN PERIODIC PRECIPITATION

BY FRANCIS E. LLOYD AND VLADIMIR MORAVEK

During our studies leading to the publication of a previous paper (1928) the authors were impressed by the wide variety of behavior and the static forms of precipitate resulting from interaction of reagents in fluids and gels to such an extent that it was determined to make as extensive a survey as possible of all systems in which periodic precipitation might occur. We believe it necessary before a comprehensive generalization can be formulated to make a broad survey and to acquaint ourselves with all possible behaviors and their results; and as such results cannot be adequately described verbally, we adopted the method of record by careful photography and cinemaphotography. Indeed the complexity of the subject is so great that nothing short of visual experience can make the variations of behavior comprehensible and especially since many authors have not made adequate records of their experiments—few of the photographs published show clearly what they are intended to show and are often very poor and unconvincing—and because most if not all papers hitherto published advance theories based on one or a few experiments with a single system only. Their authors have frequently lacked perspective to be gained only by a wide survey.

I. The Effect of Spatial Relations.

We have found that many experiments done, as is usually the case with test tubes show no periodicity for hours or days, or even not at all, whereas the same experiments done in capillary tubes show periodicity within the first few minutes of experimentation. This is in many cases due to the enhanced if also microscopic visibility due to the smallness of the masses of precipitate. Nevertheless, we have already found other effects due to the small extent of the space in which the reactions proceeded (1928) and we therefore tried to determine more exactly to what such effect might be ascribed,

Two such effects have been noticed, viz. (1) that on the rate of diffusion and (2) that resulting from adsorption on the walls, when adsorption occurs.

a. In the system NH_4OH diffusing into $MgCl_2$-gelatin we found that in the lowest concentrations no periodicity could be observed in test tubes, while in capillary tubes, well-marked, widely separated, periodic massive bands occurred. (Figs.[1] 1, 3). This is due to the slowing up of diffusion rate in the capillary tubes, which measured .5 to 1 mm. in diameter. Under these conditions the OH-ions being negatively adsorbed by the glass wall move forward in the middle of the column and the Mg-ions move radially to meet the OH-ions. The precipitate therefore takes that form of a spindle, more especially the smaller the tube and therefore the greater the curvature. In the inverse system $MgCl_2$ diffusing into NH_4OH—gelatin (Figs. 2, 4), marked irregularities also occur in both test tubes and capillary tubes, but here because the Mg-ions are positively adsorbed the bands usually fill the lumen, but are of irregular form, the negative adsorbability of OH playing a minor rôle, and, in the test tubes especially, the questionably periodic masses of precipitate are very irregular, due to local impermeability of the initial precipitate plug, and are attached strongly to the glass wall, being adsorbed thereto. In this system also the differences as between test tubes and capillary tubes are very marked; in the former usually no periodicity is observable, while in the latter it is well marked. When we repeated the above experiment, we obtained in one concentration, curiously enough, a very regular distinct band. (Fig 2a, Plate IX). This does not invalidate the general truth of our conclusions. (Figs. 1-4).

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[1] All "figs." refer to figures in the plates. Text figures are so designated.

b. Also in the system 20% NH_4OH into 2N $CoCl_2$ in 10% Difco gelatin in tubes 1, 3, 10 and 50 mm. in diameter, we found that in the narrower tubes the white precipitate was more extensive and colored bands wider and the whole diffusion column shorter than in the widest tube. In the latter there was little or no white precipitate, while in the capillary tubes the spaces between the bands were filled with it and a broad band of white precipitate was produced in advance of the last blue colored band. The tubes of intermediate diameters showed intergradations of behavior. (Fig. 8).

c. Effect of convection currents. In large tubes, because of convection currents and gravitational effects, it is impossible to obtain evidence of periodicity in fluid media. When, however, we enclosed $Pb(NO_3)_2$ diffusing into KI (or the inverse) in a very narrow space between a slide and cover glass, well marked bands of crystalline PbI_2 were obtained. (Fig. 7). The same result was obtained in .5N $Pb(NO_3)_2$ into .5N NaCl. (Fig. 110).

d. In the system .2N $Pb(NO_3)_2$ diffusing into .1N-.0125N $K_2Cr_2O_7$ in gelatin in capillary tubes 3 mm. wide it was not possible to observe periodicity except in microscopic sections. In a very thin layer of gelatin formed by the pressure of a large bubble beautiful bands were developed. In this instance the resulting forms afforded a charming spectacle (Fig. 9).

e. The trichomes of plants afford minute capillary spaces of tubular form and in such we have obtained clear and visible periodicity with the system NH_4HS into $Na_3Co(NO_2)_6$. Moreover, the precipitate occurs within the cellulose wall itself, not in the lumen except toward the end of the trichome. This can be due to the washing out of the free reagent, since the preparations were repeatedly treated with cold distilled water before adding NH_4HS (Lloyd, 1925) (Figs. 5, 6, 10). In tubes of much greater calibre periodicity occurs or at least becomes visible only after a relatively long time. (Lloyd and Moravek, 1928).

f. To be mentioned here is the example set forth by us in 1928, that in the same system as in (e) above only *rings* of precipitate are to be obtained in minute capillary tubes, whereas in larger tubes rings and discs or saturn structure are formed.

From the foregoing it will be seen that clean-cut periodicity may be procured in large spaces, but obscurely or not at all in small ones and, vice versa, periodicity may occur in small spaces and not at all in large ones. Such behaviors are indeed secondary in nature demanding special explanation, for it is clear that in many systems the tendency to periodicity is always and indubitably present but may be obscured by the special conditions present. The importance of this from a biological point of view can hardly be overestimated since many interactions must occur in restricted spaces, often of irregular shape.

The now familiar case of the "Fromman striations" on the treatment of medullated nerve fibers with silver nitrate "is the result of the operation of physical processes which in capillary spaces produce the Boehm (or Liesegang) phenomenon." (A.B. Macallum, 1906).

II. Nature of the Medium.

It has often been thought that the nature of the medium determines in a primary sense the incidence of periodicity. This, however, is not true, as many experiments in the literature, as well as our own, prove. As Doyle and Ryan correctly observe, an explanation of the phenomenon which attributes a fundamental rôle to a gel as a medium cannot be correct. We may regard this aspect of the case as a closed issue.

We cannot therefore agree with Bradford that "the nature of the gel is of fundamental importance," but rather take the position that the effect of the gel in each case must be explained and that also the rôle of the gel is a purely secondary matter. Concerning the theory of Dhar (1922) and his associates, we have to say that it assumes the presence of a gel or other *peptizing substance.* The secondary influence of the gel medium has been discussed and demonstrated experimentally very successfully by Wo. Ostwald (1926) *contra* Chatterji, Dhar and Dogadkin.

We think that McGuigan and Brough (1923/4) are mistaken when they declare that "no new chemical process is involved in the formation of rings," and when further they attach a dominant value to the dampering effect of the medium. Dampering effect there is, but it plays a secondary rôle, and it would be difficult according to their views to explain why a periodical system should occur in water and not in gelatin. See also Rouppert, whose paper contains pertinent citations (1926). Rouppert cites the important fact that periodicity can be obtained with gases only if water vapor be present, as observed by Chapin and Holmes (1918), E. Karrer (1921) and Fischer and McLaughlin (1922).

We have made use of gaseous, fluid, gelatinous and solid media. The most obvious and indeed the most important practical character of gaseous and fluid media is their instability and the consequent instability of the whole system. On the other hand, a gel supplies a framework which can stabilize the system and thus prevent mass movements which obscure or obliterate the results. This can be regarded as obvious, but it cannot be stated as a corollary that the higher the viscosity of the medium the more certain periodicity is to occur. Our experiment shown in Fig. 35 illustrates this point and will be referred to beyond under concentration of gels. Periodicity depends rather upon the amount of material (which can be expressed as dry weight) present and not at all on the viscosity of the medium.

This conclusion makes it possible to understand more clearly the comparative behavior of a particular reaction system in different gels. We have worked with gelatin, agar and starch. It is well known that agar preserves its inhomogeneity and substantial character in spite of heating at boiling temperatures, and starch still more so. We may now consider the effect of the various media used, viz. gaseous, fluid, solid and gel.

Gas:—R. B. Peet (1925) in Young's laboratory experimented with HCl and NH_3. He experienced much difficulty which we avoided by the use of capillary tubes in which the air respectively gas column is relatively stable. Without much difficulty we obtained rhythmic precipitation which settled on the glass wall. It has been observed that such periodicity demands the presence of water vapor for its realization (Rouppert, 1926) and we regard this fact important from our point of view. Since the salt formed is readily soluble and since the water vapor present puts the salt into solution soon after formation, the periodicity is quickly lost. We, however, observed its occurrence under the microscope, and were able to preserve the deposit sometimes by quickly drawing oil up into the tube. (Fig. 11).

When this system is inverted (NH_3 into HCl) the formation of periodic rings on the surface of the tube was easily observable microscopically. These were, however, quickly obliterated by extension of crystallization, so that the evidence of periodicity was quickly lost. (Fig. 12).

Any theory which attempts to account for periodic precipitation and fails to explain the above systems is inadequate. In order to do so in accordance with our views we must assume the presence of water vapor which, as we have seen, must be present if periodicity is to occur. The water vapor present, we believe, makes a temporary compound which can react with the penetrating gas. In forming the initial precipitate (the plug) water will be set free, which is now available for further reaction. Since the internal gas is highly soluble in water, the water set free moves toward the higher concentration of gas, i.e. further into the tube until a concentrated solution is formed at some distance away from the first formed crystals. The concentrated layer must now diffuse backwards to some point where it will react with the indiffusing external reagent, and a second ring will then be formed.

Fluid (Water):—It is practically less difficult, if still not easy, to obtain periodic precipitation in a fluid medium. The difficulty is overcome by employing capillary spaces. We repeated Hedges' experiments of allowing concentrated HCl to diffuse in 30% NaCl in capillary tubes. Single crystals were formed periodically and these were large enough to block, but incompletely, the mouth of the tube. Here at the moment of crystallization water is set free and it must diffuse in both directions, diluting the reagents. The space of too low concentration of the interacting reagent for crystallization must be crossed before another position of high concentration is reached by the entering reagent (Fig. 13a-c).

In the immediately foregoing experiments we do not have to consider any reaction product. Such cases are examples of periodic crystallization, the factors which prevent continuous crystallization being water and changes in temperature due to release or uptake of heat of crystallization, complicated by the formation of various crystalline modifications. In those experiments which follow a reaction product does have to be considered.

In the systems $Pb(NO_3)_2$ diffusing into KI and into NaCl in water in capillary spaces we obtained similar results, the former yielding periodic bands of crystals (Fig. 7), the latter of droplets of metastable compound which later became transformed into crystals. Notboom (1923) used this method and obtained the same results.

A most striking result was obtained with Na_2CO_3 diffusing into $AgNO_3$ in water in capillary tubes. At first the mouth of the tube was blocked by precipitate. Thereafter marked rings of metastable product attached to the glass wall appeared. In the course of three days the reaction was completed throughout the tube and we found then that, although the insoluble precipitate occurred scattered everywhere, there was a periodic accumulation of crystals in irregular bands throughout the length of the tubes (Fig. 14a-c).

In the system 1N $BaCl_2$ diffusing into 1N H_2SO_4 in capillary tubes 0.5 millimeters in diameter, rings of large crystals are formed with fewer small crystals in the interspaces. Doyle and Ryan observe that barium sulphate and silver chloride can be obtained as periodic precipitates only "with great difficulty," being very slightly soluble. Nevertheless, we have been able to do so in water. W. M. Fischer (1925) used water with a little gelatin and erythrosine admixed, and thought these to be necessary. (Figs. 16, 17, 15). Morse and Pierce (1903) got bands of silver chromate in capillary tubes in water, allowing silver nitrate to diffuse into potassium chromate.

Gels (*Gelatin, Agar and Starch*):—In the system .2N $Pb(NO_3)_2$ diffusing into .1N KI in starch and the same in agar in capillary tubes we obtained very clear cut periodicity of a yellow salt (PbI_2), but no such periodicity was obtained when gelatin was used. In the starch (Fig. 22) there was a strong tendency toward irregularity, spirals and other abnormalities appearing, or even a discontinuous band of granules representing the continuous bands elsewhere. Also here, since the salt was strongly absorbed on the glass wall the ring-and-disc structure was pronounced. In the course of time the yellow salt, which has here a metallic lustre, is dissolved or is hydrolyzed, or otherwise changed, and a product is set free—probably I_2—which produced a purple coloration in the starch medium, the color being deepest where the yellow salt had occurred.

When potato-starch is used instead of the much finer grained corn-starch, no continuous bands are formed. In their place we find a periodicity in the form of discontinuous zones of crystals. These appear even at the very beginning of diffusion. It is also interesting to note that the release of I_2 is much more rapid, so that the yellow salt quickly disappears and the starch becomes colored.

In agar beautifully regular and clean cut ring-and-disc bands or spirals occurred in harmonic periodic array, which were dissolved in the entering reagent as the higher concentrations advanced into the tubes. (Figs. 18, 19).

Hatschek (1921) and doubtless others (Dogadkin) observed the formation of spirals following the addition of acetic acid to the entering reagent. We have, however, repeatedly found that spiral structures are likely to occur in at least one in a dozen tubes under the same circumstances, and we have particularly observed that a small bubble attached to the surface of the medium, locally preventing diffusion at a small point, will induce the irregularity of the first precipitation membrane or surface of the precipitation which will by repetition give rise to a spiral (Figs. 19, 22).

In gelatin at first a yellow, continuous column was formed (Fig. 21). This disappeared as the concentration of the entering reagent increased and the presence of a vitreous, probably organic, precipitate of a colorless salt in the form of globuloids was apparent. As the precipitation advanced, rings appeared independently in the yellow precipitate, which became more and more visible as the yellow precipitate disappeared. These were insoluble in the entering reagent and were composed of an apparently vitreous mass with a cloudy milky-white interior (Fig. 21a). We must here point out that the medium cannot be a simple mechanical framework in these and possibly other cases and we have always to consider the possibility of the gelatin, at least, entering into the reaction in some way both here and in regard to other systems in gelatin. Indeed recent work done by one of us strongly supports this idea, but the limitations of this account prevents us from exposing our further evidence here.

The system $AgNO_3$ diffusing into $K_2Cr_2O_7$ with gelatin, with agar and with starch. (Figs. 20, 25, 26). In these cases there is no evidence that there is other than mechanical action of the medium. Periodicity occurs in all three, but more clearly cut and regular in gelatin and least so in agar. In starch there appears to be no evident protective action so that a precipitate of coarse, dark red crystals appears, the coarser the further away from the mouth of the tube. Here also the periodicity may be absent or may appear in quite clear-cut and evident fashion for a short distance only. Periodicity is most likely in these cases to occur at low concentrations of the entering reagent.

In gelatin and agar, two salts, red and yellow (Ag_2CrO_4) and a complex between this and $K_2Cr_2O_7$ respectively, always appear. In the gelatin both are sharply periodic; in agar only the red is periodic. As the concentration of the entering reagent increases the yellow rings become red and this indicates that the complex is split and that the products proceed in the direction of Ag_2CrO_4.

In agar the yellow salt does not as readily pass into the red salt, the protective action of agar being less than that of gelatin, so that in the former large crystalline masses build up vague red bands of irregular cloudy form without sharp edges as viewed laterally (Fig. 25).

The system $HgCl_2$ diffusing into KI in starch, in agar and in gelatin (Figs. 27-30). In starch, large red crystals were first formed in a broad band laid down with an evident but not strikingly obvious periodicity followed by a broad band of large, feathery, yellow crystals shot through with long, acicular red crystals with no evident periodicity, these in turn followed by fine red crystals in which a well marked fine periodicity occurred, more evident at greater length. The starch here formed a mere mechanical medium and had only slight or no protective action (Figs. 27, 28).

In agar a more pronounced but still low protective action occurred. Fine red crystals were first formed, but later yellow, in which a fine-grained but definite periodicity occurred (Fig. 29).

In gelatin a chemical action on the medium occurs. This shrinks transversely, leaving the glass wall as the concentration of the entering reagent increases; diffusion is much retarded and periodicity does not occur, or is, at any rate, extremely vague (Fig. 30).

The system $Pb(NO_3)_2$ diffusing into K_2CrO_4 in starch, in agar and in gelatin. All three afforded a very well defined periodicity. Here these media accidently so to speak, have no chemical action and have nearly the same mechanical action toward the precipitate (Figs. 31, 32, 33, 51, 52, 57).

When the foregoing systems are inverted, no evidence of any periodicity at any concentration is obtained in agar or gelatin, while in starch a very sharply defined regular periodicity occurs (Fig. 24, 112, 113).

It is evident that this system is very complicated, since periodicity appears in one direction of diffusion and not in the other. It is noteworthy that starch is here the one medium which affords periodicity for K_2CrO_4 when diffusing into $Pb(NO_3)_2$. It may be a question of diffusion.

When the conditions are the same except that dichromate is substituted for chromate, periodicity is obtained in all three media but is better developed in agar than in starch and still better in gelatin. We shall endeavor to offer an explanation of the above in the discussion beyond (Figs. 23, 34, 80).

The system 20% NH_4OH into 2N $CoCl_2$ in gelatin, for which the gelatin was liquified at a low temperature (50 deg.C) at concentrations of 5, 7 and 15% of gelatin. In no case was periodicity observed. At the lowest concentration (5%) of gelatin, a broad band of white precipitate precedes the blue precipitate. In 7% the white band is not so pronounced and is only slightly apparent in 15% (Fig. 35).

If the 25% gelatin is liquefied and used at once for making up the internal complex, bands do not appear as quickly as when the gelatin is kept for 30 seconds at 100 deg. C. If, on the other hand, exposure to this temperature is sustained for two hours the result becomes complicated by the production of white precipitate and the periodicity of the blue salt is quite irregular (Fig. 36).

It is evident here that gelatin is changed by the treatments indicated and that the resulting changes are reflected in the character of the periodicity.

In the same system the importance of the concentrations of gelatin is brought out by an experiment in which it varied in concentration from 15% to 3% in eight steps. In all concentrations the diffusion is constant until periodicity appears, which happens earliest in the highest concentrations when the bands formed hinder the diffusion rate (Fig. 37).

In agar (.5 to 2.5%) the same relation holds.

Solid Media:—Various observers have obtained periodicity in solid media of divers sorts. We tried gypsum with the system .2N $AgNO_3$ diffusing into .05N $K_2Cr_2O_7$ in a capillary tube. The progressive reaction was made apparent by the appearance of small dark red crystals of Ag_2CrO_4. There was evident periodicity, lacking however obvious harmonic arrangement.

Summary and Theory

In our previous paper we argued that every reaction can proceed periodically. We now hold that it can be obtained in every kind of medium if the necessary conditions of space and concentration are supplied. The exceptions are to be found in those cases in which a reagent has reacted with the medium or in which the gel fails to act as a protective colloid for the precipitate. Even then periodicity may occur occasionally.

The medium can act chemically or be purely passive in this regard and so act merely mechanically.

Viscosity plays a very minor rôle in influencing diffusion.

In higher concentrations of the medium, however, more periodicity occurs than in the lower.

III. Effect of Surface.

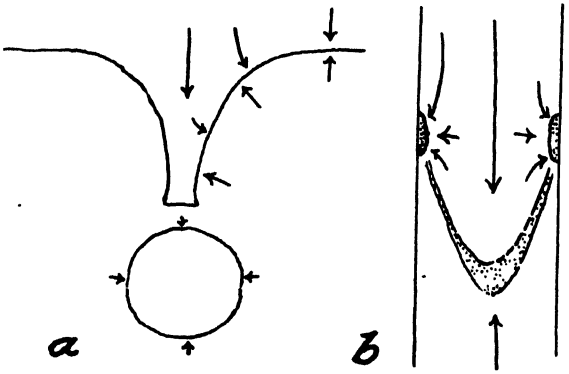
a. The surface of the tube, etc., enclosing the system.

We have already indicated in our previous publication the rôle played by the surfaces of the enclosing vessel. The principle is further illustrated by the following additional observations.

The system Na_2CO_3 diffusing into $AgNO_3$ in capillary tubes. In this reaction coarse crystals are formed which attach themselves on minute irregularities on the inner surface of the tube. These are minute areas of high curvature caused during the blowing of the glass tube, as shown by the fact that the crystals are attached in parallel lines running lengthwise inside the tube. As long as the saturation of the salts resulting from the reaction is too low, scattered crystals only occur. When the saturation is sufficiently high, a ring of separate lines of crowded crystals is formed, the whole picture showing periodicity. In this case the reaction product is very strongly positively adsorbed on the glass wall. If this were not the case the precipitate would be distributed as a diffuse, vague cloud of particles in the corresponding zones (Fig. 14a-c).

The system K_2CrO_4 diffusing into $AgNO_3$. In this case we give one in which the concentration of the reaction product is too low to supply sufficient material to form a complete band. Since here the precipitate is very strongly adsorbed on the glass wall, it attaches itself to the minutest irregularities in periodic fashion. Since the irregularities of the same order of magnitude occur in a particular line, the clumps of precipitate are to be found along this line, of two or more. If the precipitate is not positively adsorbed it will be found scattered throughout the whole medium and no periodicity might then be observed (Figs. 38, 39).

In the case in which oversaturation occurred, as in the system 2% $K_2Cr_2O_7$ diffusing into .5N $AgNO_3$ in gelatin, the reaction product, being strongly positively adsorbed on the glass wall, is deposited in a dense ring which so far depletes the corresponding transverse zone that a reaction of oversaturation is reached only in advance more or less of the already deposited ring. Thus is formed a disc corresponding to the ring (Text Fig. 1b.) This is the "saturn structure," so called by Popp. We must accordingly always find the disc to be laid down somewhat later than the corresponding ring and this, more easily in the greater depths of the tube, can be seen to occur, the ring being formed some time before the disc. The time interval increases the deeper in the tube we go. Between the rings the precipitate is formed more slowly, due to the low saturation as the entering reagent advances and it is deposited on the glass wall. If in sufficient amount it may entirely obscure the periodicity (Figs. 40, 41, 44-46, 77).



TEXT FIGS. 1a AND 1b

Since adsorption will play a greater rôle in small tubes, it becomes less important in large tubes in which the surface therefore will play a minor rôle. The deposit of precipitate will go at once to the disc and the ring is not formed appreciably earlier.

In order to explain the ring-and-disc structure Dogadkin has postulated a curved surface (meniscus) of the medium where the external reagent enters. In order to assure this structure, the meniscus must be concave. This view is quite without foundation, as we have been able to obtain the ring-and-disc structure when the meniscus in question was curved in the opposite sense. It is, furthermore, absent when the precipitate formed is negatively adsorbed on the glass wall.

We tried to determine if the kinds of material would have any effect, using the system 20% NH_4OH diffusing into 2N $CoCl_26H_2O$ in 10% gelatin in tubes 10 millimeters in diameter of the following materials: silica, soft glass, hard Jena glass, chemical glass tubes lined with caoutchouc, collodium, cacao butter, paraffin and lecithin. In all, the rates of diffusion and the number of rings were the same (Fig. 47).

Summary: The surface plays an important rôle in capillary tubes, but a less important or even negligible rôle in tubes of larger diameter. Accordingly we may obtain periodicity in the former, but not in the latter. The relative importance will depend on the nature of the precipitate or on the degree of adsorption.

Wulff (1929) had investigated the deposition figures of iodine *in vacuo* and found the first deposition always in places where there are minute curvatures, scratches and tension lines on the glass surface. We have observed the same and have offered evidence in many of our illustrations. Such minute irregularities as Wulff speaks of can account for many appearances in the case of substances adsorbed on the glass wall unexplained otherwise.

b. Surfaces in the medium, inhomogeneity.

The following interesting behavior took place in the system .25N $AgNO_3$ diffusing into .25N NaCl in gelatin in test tubes. The preparation which was observed during two months, yielded at first a very fine periodicity observable only through the microscope and later broad bands with no interspaces appreciable to the eye, so that the bands could not be distinguished until the preparation was exposed to the light, when a differential blackening, due to difference in densities, occurred. The preparation had been kept in the dark. During the period, fungus hyphae developed in the column of gelatin beyond the precipitate and when these were overtaken by the reacting salt a microscopically coarse crystalline precipitate was deposited (AgCl), which, being negatively adsorbed on the glass wall, was scattered throughout the medium. It was, however, positively adsorbed on the fungus hyphae so that the form of the fungus was made evident by the crystals attached to it. (Fig. 48).

Appearances in the system $AgNO_3$ diffusing into $K_2Cr_2O_7$ in gelatin when the experiment is carried out in the classical fashion of Liesegang, i.e. when a drop of the entering reagent is placed on a field of $K_2Cr_2O_7$—gelatin in a glass plate (preferably a Petri dish so that it may be protected from evaporation the more easily). Under these conditions three sets of rings (here well enough so called) are produced, not two only as usually supposed. First a set of fine colorless rings (regarded as phosphates by us). These are produced with great regularity and uniformity until at some distance from the center of diffusion they lose all regularity and periodicity is quite lost. On the colloidal suspension forming the precipitate of these rings, a second dark red silver chromate set is formed by adsorption but the regularity of these is disturbed by the loss of regularity of the primary rings and more or less by the presence of various foreign bodies (minute fibers, particles, etc., etc.) in the gelatin. The rings of the third set are brown and ribbon-like, occurring only at the *gelatin-air interface* and while obviously related to the second set, to some extent are independent. Such rings do not occur at the gelatin-glass interface and are evidently circumstanced by the presence of the gelatin-air interface, *which does not occur in tubes.* If a sheet of thin glass is placed on the gelatin so that the radially extending diffusion must pass partly under the glass, this system of rings is formed only at the gelatin-air interface up to the edge of the glass cover, beneath which it is not to be found, though there is some scattered granular material adsorbed at the gelatin-glass interface, due especially to dirt, etc. on the glass. It becomes apparent that we are here dealing with the saturn structure which occurs only as above described, viz. when a gelatin-air interface is available.

The ribbon-shaped ring can occur, if the layer of gelatin is thin, without any accompaniment of precipitate inside the gelatin, just as the ring alone may occur in a test tube beyond the rings-and-discs.

In our previous paper we have referred to similar conditions procured experimentally.

Fungi, of course, grow readily on some media. In .2N Na_2HPO_4 diffusing into .5 to .006N $CaCl_2$ in test tubes, the preparations of which were observed during the period of a month, there occurred an abundance of fungus colonies which grew in spherical form. Since in this case the reaction product was negatively adsorbed on the fungus, the dense spherical colonies merely formed barriers which hindered the diffusion of the reagents, more or less, according to the position of the colony with regard to the band being formed. The forms of the precipitate were therefore determined by the new directions of diffusion, affording curious funnel- or dome-shaped irregularities in the disc of the ring-and-disc, which latter as a whole is referable to the positive adsorption on the glass wall (Figs. 42, 43, also text Fig. 1a).

With the system $Pb(NO_3)_2$ diffusing into K_2CrO_4 (.5N into .1 to .0031N) in agar in capillary tubes we obtained quite unusual and at present inexplicable results. For the most part the resulting periodicity consisted in fine regular bands of very fine precipitate not adsorbed on the glass wall. In one tube of the highest concentration of entering reagent two periodic systems became visible (a) a relatively coarse band, each band preceded by an interspace relatively free from precipitate and (b) fine banding locally confined to small columns of the medium, being absent elsewhere. In a transverse section we found that there was a very irregular distribution of precipitate, rather obviously connected with a considerable inhomogeneity in the material of the medium. A section from another tube in which the fine bands were uniform and spanned the whole lumen of the tube, showed a quite different picture, only very minute irregularities appearing (Figs. 49, 50, 51, 52).

It is much more likely that starch should produce such irregularities if prepared so that the grains are incompletely hydrated, when nuclei poor in water will occur suspended in a colloidal mass of more highly hydrated starch. Systems especially in which there is a delicate equilibrium between periodicity and non-periodicity are easily upset in starch while in agar and gelatin they afford very regular pictures. This is especially well shown in the system $Pb(NO_3)_2$ diffusing into KI in corn starch paste (Figs. 19, 22).

When potato-starch (Fig. 22, three right hand tubes), with its much larger grains, is used, while periodicity is produced, especially in finer capillaries (.2-4. mm. diameter) the precipitate consists wholly of coarse crystals and there occur no continuous bands such as we see in the five left hand tubes of Fig. 22.

By introducing certain adjuvants to the medium we have changed the surface tension of the minute components (micellae, granules) of the medium and we have sought to determine the effect that such additions would have on the periodicity of the system when substances which lower the surface tension were introduced. The following substances were used and the corresponding surface tensions at the air-water interface as determined by means of a de Nouy tensiometer are given as follow:

1%	Sodium oleate		surface tension 37.3
.1%	do.		41.1
	Capryl alcohol	saturated solution	55.5
.1	do.	do.	56.9
.3	Cholesterol	by the Moravek method	42.2
.03	do.	do.	47.8
.003	do.	do.	not measured.

These were added to $CoCl_2$ in 10% gelatin. In sodium oleate and cholesterol the banding was identical with that in distilled water, the control. In capryl alcohol in both solutions there was a considerable departure from the control in the great prominence of white precipitate with few and diffuse blue rings. We must assume a chemical interaction in the case of the capryl alcohol, for it is clear that the changes in surface tension had no effect (Fig. 53).

Macro-inhomogeneities, as in starch and agar (especially when prepared by partial hydration), affect the behavior of the reagents and of the precipitate in any system.

IV. Final Form of the Precipitate.

Crystalline precipitate. The precipitate occurs in the form of crystals (micro and macro) in water and in media which do not act protectively and which therefore behave, aside from purely mechanical support, as if not present; e.g. 2% $CaCl_2$ diffusing into 2% $(COONH_4)_2$ in gelatin in capillary tubes. Here no trace of periodicity was visible. The crystals were small placques, single or aggregated into small spherocrystalline groups. In the inverse of this system we obtained at first small crystals which became larger the further in the tube where the diffusion was slower. A very slight indication of periodicity was evident in one or two tubes e.g. the right hand tube, Fig. 55. (Figs. 54, 55, 72).

The precipitate may be at first diffuse and suddenly pass into a periodic condition if the entering reagent is hindered from rapid diffusion as e.g. by a bubble (Fig. 57). Whereas in the system $K_2Cr_2O_7$ diffusing into $AgNO_3$ in starch (.5N into .1 to .0031N) we observed all intergraduation between periodicity and nonperiodicity (Fig. 56).

In the system $Pb(NO_3)_2$ into NaCl in gelatin (.5N to .25 into .5 to .25N) we obtained periodic bands of spheroidal crystals which very slowly developed from the already laid down colloidal precipitate (Figs. 58, 59).

It is evident that periodicity is not at all conditioned by the colloidal state of the precipitate as we obtained well defined periodicity in many experiments in which the salts formed are hardly to be obtained in colloidal form, as in the case of $BaSO_4$ in water (Figs. 15, 17).

Colloidal precipitations: growth forms. In the systems $K_2Cr_2O_7$ diffusing into $AgNO_3$ in starch (.5N into .1 to .0031N) we obtained the reaction product in the form of semi-permeable cells, more or less in periodic grouping. We recognized these as Traube membranes, which grew in size after breaking out and producing various curious and fantastic shapes (comma, comet and other). We removed some of them, mounting them for microscopic examination in the entering reagent, when on crushing we could observe the formation of new membranes and the growth of older ones (Figs. 60-64). Similar, very uniform, comet-shaped membranes were obtained in 50% $AgNO_3$ diffusing into .5N $K_2Cr_2O_7$ in gelatin in a glass plate. The thinness of the gelatin was here a factor (Fig. 60, inset). *Sharp banding.* The reaction product according to rate of diffusion and of concentration yielded different forms of colloidal precipitate in the two main types of diffuse and sharp (Figs. 65, 67, 68). These appeared, e.g. in the systems $(NH_4)_2HOP_4$ diffusing into $CaCl_2$ in gelatin (.2N into .1 to .006N) and NH_4OH diffusing into $MgCl_2$ in gelatin, as also in some other systems. Popp (1925) obtained bands in the system ammonia and magnesium chloride in both directions, whereas we obtained bands usually only when the ammonia was the entering reagent. Once, however, we got the same result as Popp when 0.5 sat. soln. MgCl diffused into 1N NH_4OH in gelatin. (Fig. 2a, Plate IX) This does not, however, militate against our view. We used various concentrations of gelatin and our results were the same as hers, so far as they go.

In 4% $Pb(NO_3)_2$ into 4% KI in gelatin we obtained a yellow colloidal cloudy periodic precipitate which was changed on the increase of concentration of the entering reagent to white granules which grew into spheroidal crystals grouped periodically (Fig. 66). There is difficulty in the interpretation of Pb and Ag reactions in gelatin. As is well known, Pb $(NO_3)_2$ with gelatin alone afford a periodic precipitate negatively adsorbed on the glass wall. If tubes are thus set up as control, similar tubes with KI give, in addition, a cloudy colloidal yellow precipitate with a sharply banded white periodic precipitate within the yellow.

We have already pointed out that when the precipitate is colloidal and positively adsorbed on the glass wall (or other suitable interface) the ring-and-disc structure always appears. Whether it is well defined and regular or ill defined and irregular or otherwise depends on secondary conditions, especially on diffusion rates. Bradford's observations (1919) on the adsorption of a cloudy or colored precipitate in the region of the band accords with ours but does not militate against our theory.

Periodicity is evidently independent of all possible states in which the reaction product may occur. The problem of periodicity then is to be solved quite in disregard of these conditions, contrary to some theories which have been advanced.

Influence of one precipitate on a second. Phosphates in the gelatin. System $AgNO_3$ diffusing into Na_2HPO_4 and inverse (Figs. 71, 73, 86). When we experimented with these we found in all cases two systems of rings, one of fine bands in advance and, adsorbed on these, a second dark appearing precipitate. We attribute these fine rings tentatively to phosphates in the gelatin, chlorine being absent. They are developed most abundantly and uniformly in the lower concentrations of the internal reagent. In the higher concentrations the fine rings were more poorly developed and coarse spheroidal masses showing weak or no periodicity took their place. In certain intermediate concentrations we obtained intergrading conditions, in which the coarse precipitate was adsorbed on the finer.

In experiments in which $AgNO_3$ is allowed to diffuse into gelatin without additional reagent a fine periodic precipitation is obtained and this, when other reagents are added, forms a groundwork for the additional precipitate to be adsorbed upon. Stansfield (1917) also observed a microscopical periodicity in the system silver nitrate diffusing into K-chromate. In the plug it had the same periodicity as the chromate. This groundwork again seems to be due to phosphates in the gelatin. When NaCl is added to the gelatin a different and much finer periodic precipitation is obtained with readiness recognizably different from phosphate rings which are more soluble in the entering reagent than the chloride. Liesegang examined the behavior of silver nitrate diffusing into potassium chromate-gelatin and the inverse, observing the fine white bands which he attributed to chlorides, which, however, he stated as not being necessary to the formation of the chromate bands and as not present when the chromate diffuses into the gelatin.

Nor are they present when the medium is prepared by adding $AgNO_3$ to the gelatin, followed by $K_2Cr_2O_7$, (and therefor containing the reaction product, but neither free chlorides or phosphates). The excess $K_2Cr_2O_7$ reacts with the entering $AgNO_3$ periodically, but no fine banding is seen (Fig. 71a).

Lagergren (1899) observed negative adsorption of NaCl and Bradford on the addition of this to $K_2Cr_2O_7$-gelatin obtained only diffuse cloudiness with $AgNO_3$, whereas we have found clear cut periodicity.

We agree to some extent with Bradford that there is something either already present in the gelatin (impurities, he calls them) or, as we have already suggested, which appears in the course of the reaction periodically as fine bands facilitating the periodicity of the chromates of Ag and Pb, but which assuredly is not a *sine qua non.* If mineral impurities are present we argue that they are phosphates since we obtain similar periodicity when Ag or Pb diffuses into gelatin containing phosphate (Figs. 70, 71, 74, 75). On the other hand we admit that the fine bands may be due to a reaction of Ag or Pb with the gelatin itself.

When $Pb(NO_3)_2$ diffuses into gelatin alone a mixed cloudy and coarse periodic precipitation is formed, the latter composed of spheroids of pearly appearance. When K_2CrO_4 is added to the gelatin the chromates, being weakly developed at low concentrations of the internal reagent, form insufficient surface for the adsorption of the phosphates and these are then present as scattered globulites. In the higher concentrations of chromates the very numerous bands present allow the full adsorption of the phosphates, which are then periodically deposited thereon (Fig. 33).

It should be added as confirmatory of the foregoing statements that we never obtained the precipitation of phosphates in agar alone or in starch alone. Also we obtained with the system $Pb(NO_3)_2$ diffusing into K_2CrO_4 in agar the same fine bands, which we attribute to chromates, as we did in the above mentioned experiment in which such bands serve as a groundwork for the emplacement of the coarser phosphate precipitation (Fig. 57).

Summary: There can be at least two sets of periodic precipitation in a single system. When one is adsorbed positively on the other the appearances are complicated and are different according to the concentrations of the reaction products.

V. *Influence of Concentrations.*

(a) *Silver chromates.* System K_2CrO_4 diffusing into $AgNO_3$ in 6% gelatin (.5N into .1 to .0031N). In the highest concentrations complete rings with discs are formed in sets of 2 to 4. The earlier formed rings have their accompanying discs, the later have no discs; the material being entirely used in forming the rings. This results from the reduced rate of diffusion and concentration allowing time for all the reaction precipitate to be adsorbed on the glass wall, at least for the most part. Whenever the disc fails to be formed in addition to the ring on the glass wall there are always scattered granules of precipitate in the interspaces due to the presence of local adsorption centers. In the lowest concentration of internal reagent in which any precipitation occurred (.0125N) the whole of the reaction precipitate is adsorbed on the glass wall. Either entire rings are formed or, as is usually the case, only clumps of precipitate, attached to irregularities on the glass wall, form rough and irregular rings. In extreme cases when the tube is too large the precipitate will be entirely on the glass wall and may show no periodicity at all. At medium concentrations the ring-and-disc structure is marked and generally regular, showing, however, minor irregularities of structure (incomplete rings, gaps in the discs, etc.). Most important, however, is the fact that the discs are always bowl-shaped with the convex surface inwards (directed away from the mouth of the tube). This is to be explained by changes in the concentration of the reagent due to its rich and very rapid accumulation on the glass wall (Fig. 77).

In the inverse of the above system, viz. in $AgNO_3$ diffusing into K_2CrO_4 in gelatin there is laid down a set of phosphate bands (in the inverse system the phosphates are already precipitated by mixing with $AgNO_3$) upon which and upon the glass wall the chromate reaction precipitate is strongly adsorbed. As Davis (1922) correctly suggests, the opaque bands (which we call phosphate bands) extend from the beginning of the precipitation column and do not delay their appearance to some time after the process begins, in the case of silver nitrate diffusing into chromate-gelatin. In the highest concentration periodicity of chromates is not established for some time. In this and in medium concentrations rings and discs are first formed giving place more or less quickly according to concentration to rings alone and finally to granules scattered more or less periodically.

As Stansfield (1917) observed, however, the banding in silver chromate extends much further into the plug, as a fine microscopic structure, than is detectable by the eye. In the lowest concentration the periodicity of the chromate became cloudy and vague but regular and quite evident, the small amount of chromate being adsorbed on a large number of phosphate bands (Fig. 76).

Stansfield (1917) studied silver nitrate diffusing into K-chromate and the inverse, finding little difference, as had also Liesegang.

In the same chemical system but with agar instead of gelatin, the phosphate bands being absent, the chromate alone is precipitated periodically as minute colloidal spheroids with much precipitate in the interspaces. The bands are broadest in the higher concentrations and are scarcely present at all in the lowest (Fig. 78). When we repeated the experiment with a poured agar plate (instead of tubes) we could observe a colorless but non-periodic zone preceding the red precipitate, which occurs first as a cloudy precipitate roughly, but evidently periodic, which quickly becomes irregular. This irregularity is owing to the quick formation of centers of low vapor tension, that is, adsorption centers, which grow at the expense of neighboring smaller centers. It is adsorption of the salt on such centers which discomposes the disposition of the precipitate in regular periodic fashion. The presence of a fiber disturbing the periodicity in Fig. 103a exemplifies this. Lastly, when starch is substituted for agar somewhat coarser crystals are obtained, coarsest in the highest concentrations with no trace of periodicity (Fig. 76b). When, however, we invert this system (K_2CrO_4 into $AgNO_3$ in starch) similar crystals are formed but a good periodicity is obtained, very sharply defined in the higher concentrations but absent from the lowest. The rate of diffusion is as usual more rapid in the lowest concentrations of internal reagent (Fig. 56).

System $AgNO_3$ into $K_2Cr_2O_7$ in gelatin. The diffusion rate is highest in the lowest concentration of internal reagent, as Stansfield observed (1917). Very regular phosphate periodicity occurs in all concentrations equally. The chromate is laid down periodically and is adsorbed on the phosphate bands. Each band of chromate is compound of one to several phosphate bands carrying the chromate according to the distance from the mouth of the tube. Irregularities of chromate deposition are not referable to deposition between the phosphate bands, but to irregular and scattered deposition on the regular phosphate bands, which themselves become irregular at length and this increases the confusion. It is important to note that here the chromate is negatively adsorbed on the glass wall. We have already pointed out that it is positively adsorbed at the gelatin-air interface (Figs. 74, 79).

Liesegang (1914) has thought of the possibility that there are two modifications of silver chromate of which one makes the diffuse precipitate and the other the rings and that the one has no "*Keimwirkung*" on the other. We have thought the same, but we do not find any need for bringing the factor of *Keimwirkung* into account.

In starch and agar there are, of course, no phosphate rings and while periodicity of the chromates is evident it is not at all so sharply defined and although more evident in some concentrations it may be vague or scracely observable in others (Fig. 26).

System $AgNO_3$ diffusing into $K_2Cr_2O_7$ in starch, the inverse of the immediately foregoing. No phosphate bands are present and no periodicity of the chromate occurs in the highest and lowest concentrations. In the medium concentrations well developed periodicity of coarse granular precipitate of growing Traube membranes occurs (Fig. 82).

(b) *Lead chromates.* System $Pb(NO_3)_2$ diffusing into K_2CrO_4 in gelatin. Here the phosphates do not afford bands but merely white sphero-crystals. The lead chromates are not adsorbed on the phosphates and therefore effect a regular independent periodicity. The phosphates, on the contrary, are adsorbed on the chromates and in higher concentrations form irregular clumps attached to the chromate bands, smaller and smaller as the concentration of chromate is lower (Fig. 33).

System $Pb(NO_3)_2$ diffusing $K_2Cr_2O_7$ in gelatin. A deep lemon yellow crystalline precipitate always occurs, coarser in the higher and finer in the lower concentrations of internal reagent. Immediately within the first few minutes of diffusion periodicity becomes evident; regular narrow bands with interspaces filled with more scattered crystals, the more regular and numerous in the lower concentrations. The periodicity soon fades away and the precipitate then becomes continuous (Figs. 34, 80).

In the course of a week a second periodicity makes its appearance, this time of a few broad bands more lightly colored, or more numerous narrower bands, so that always there occurs two periodicities, the one early the other late. We may perhaps attribute the latter to the presence of sulphates, the S_2 being derived from the gelatin, as we found to occur previously (1928) (Fig. 80).

Systems $Pb(NO_3)_2$ diffusing into K_2CrO_4 in agar and the reverse. In the former a very fine and regular periodicity occurred in all except the lowest concentration. In the latter there was no periodicity at all, beyond a very fine microscopic periodicity in two of the tubes (.05N and .025N) (Figs. 49, 50, 51, 52, 112, 113).

In the same systems with starch as medium. A fine periodicity of the same general character as in agar occurred in both. In K_2CrO_4 diffusing into

$Pb(NO_3)_2$ the reaction product appears to be negatively adsorbed on the glass wall but in its inverse positively (Figs. 24, 31).

(c) *Phosphates.* a. System Na_3PO_4 diffusing into $CaCl_2$ in gelatin. Near the open end of the tubes there is an appearance of periodicity. The rings are of cloudy precipitate but are irregular and somewhat vague. From the very (open) end of the tubes crystal masses are present and show a gradual gradient in dimensions until they reach a critical size, after which periodicity disappears.

Periodicity appears only in the highest concentration used, probably because the triphosphate is too alkaline and is neutralized partly because of the acidity of the 1N solution $CaCl_2$ (Fig. 81).

b. Na_2PO_2 diffusing into $CaCl_2$. In all concentrations white phosphate bands strongly adsorbed on the glass wall are formed. In the higher concentrations the interspaces are filled with metastable crystals which evaporate and give up their material to the rings and discs (Figs. 83, 84).

c. $NH_4H_2PO_4$ diffusing into $CaCl_2$ in gelatin. In the highest concentrations coarse spheroidal crystals are first formed without periodicity, after which periodic rings strongly adsorbed on the glass wall appear. Each ring and disc is formed at the inner limit of a periodic group of crystals. In a lower concentration (.05N) only crystals appeared without periodicity and no precipitate at all occurred in still lower concentrations (Fig. 85).

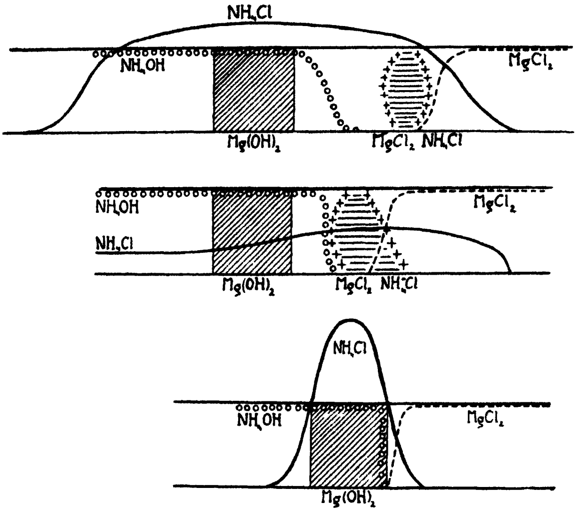
d. $(NH_4)_2HPO_4$ diffusing into $CaCl_2$ in gelatin. Spheroidal crystals appeared without periodicity in the upper three concentrations, more in the highest concentration. At the same time rings of colloidal precipitate were formed, strongly adsorbed on the glass wall, and these grew at the expense of the crystals. In the lower concentrations only colloidal precipitate forming ring-and-disc structure were formed. The rings were broader and denser toward the depth of the tube. The discs (Fig. 69) were curiously irregular (Figs. 67-69).

e. .1N $AgNO_3$ diffusing into .1 to .0035N Na_2HPO_4 in gelatin. In the lower concentrations there occurs the same fine periodic precipitation which occurs in every case in which $AgNO_3$ diffuses into gelatin, viz. fine phosphate bands. With increasing concentration the fine bands are reduced in number till in the highest none appear. A second precipitate is also present in the higher concentrations in the form of coarse spheroidal masses which decrease in size with the decrease of concentration (.0031N and lower) and in which there is no periodicity until the particles become of colloidal dimensions when they are adsorbed upon the fine bands in a sharp periodicity which, however, becomes vague and cloudy, if still evident, in the lowest concentration (Figs. 71, 86).

The failure to produce bands in the higher concentrations appears to depend on the formation of a difficulty permeable plug at the mouth of the tube, which naturally lowers the diffusion rate. In consequence also the coarse precipitate noves forward in the higher concentrations only very slowly. We must assume both kinds of precipitate to be modifications of the same salt.

The inverse system Na_2HPO_4 into $AgNO_3$ in gelatin. Periodicity was observed only in the four higher concentrations. The precipitate is colloidal and very strongly adsorbed on the glass wall and a long initial plug in the three higher concentrations (.2 to .05N) has no periodicity. In the highest concentration the bands were broad, regular but vaguely delimited, more irregular in .1N while in .05 it became a lobulated strand. In .025N the periodicity was fairly regular and the precipitate very fine. We note again the adsorption on the glass wall of the reaction product in one case but not in its inverse. With time a secondary change overtook the primary precipitate and spheroids were formed at the open ends of the tubes, showing little if any periodicity (Fig. 73).

System .5N ammonium oxalate into .1 to .0031N $CaCl_2$ and the inverse. In both a crystalline precipitate occcurred without any periodicity. In the former the crystals are large and become feathery progressively toward the depth of the tube. In the latter the precipitate was extremely fine, nearly colloidal. In both the size of the particles diminished with concentration. In the case of an insoluble precipitate being at once formed, periodicity appeared with great difficulty, if at all (Figs. 54, 55).



TEXT FIG. 2

Experiments in test tubes. System NH_4OH diffusing into $MgCl_2$ in gelatin. Here the diffusion was more rapid in the high concentration of the interval reagent than in the lower, contrary to our other experiments (Figs. 1, 3).

Hedges (1928) showed that the outward diffusion of ammonium chloride is not essential to the production of periodic structure in the system ammonia-magnesium hydroxide-gelatin. The outward diffusion of the reaction product can in any event be outward only from the place of highest concentration and must be inwards also from this point. We believe that this inward diffusion leads to the formation of a complex with the reagent already present, which in turn diffuses outwardly (text Fig. 2).

The theory of Bechhold as cited by Hedges postulates three diffusion waves, those of the two reacting substances and that of the soluble product. Our view also demands three—that of the entering reagent, the reaction product and the complex which arises when the concentration of the inwardly diffusing reaction product becomes high enough to form this complex with the internal reagent. This complex will now have an independent diffusion carrying it back to meet the entering reagent at a new point to which by this time the entering reagent has traveled. A new lot of reaction product is then formed and behaves similarly.

Fricke and Suwelack (1926) point out that E. Weitz (1924) has shown that Mg-salts in a concentrated solution of ammonia containing ammonium chloride, amine complexes are formed, and they used this to explain the formation of Mg-hydroxide rings, which are less soluble in the higher concentrations of ammonia. They say that this is an exceptional case in the formation of rings, but we take the view that every periodic phenomenon must be preceded by the formation of a complex salt.

System $MgCl_2$ diffusing into NH_4OH see p. 1530, 1543.

System NH_4OH diffusing into 2N, 1.5N, 1N and .5N $CoCl_2$ in 20% gelatin. The rate of diffusion of the entering reagent is slowest where the concentration of the interacting reagent is highest and vice versa. Where diffusion is slowest periodicity is earliest to appear. In the lower concentrations the precipitate is dissolved by the entering reagent and more rings are formed in the higher concentrations than in the lower (Fig. 91).

The same system but altering the concentration of the entering reagent, viz. NH_4OH 10, 15, 20 and 25% into 2N $CoCl_2$ in gelatin. The higher concentrations of the entering reagent diffuse more rapidly than the lower and the periodicity is more developed in the higher than in the lower (Fig. 90). The same system with agar instead of gelatin. The diffusion rates are the same as for gelatin. The periodicity in the lower concentrations begins closer to the mouth of the tube and the bands are more diffuse and broader than in the higher (Fig. 89).

Summary. At higher concentrations of the internal reagent there is a tendency for a plug to be formed at or near the mouth of the tube and the entering reagent is also used up more rapidly, reducing the rate of speed at which it reaches the depths of the tube. In the majority of cases therefore, the slowest diffusion is in the tubes of highest concentration of the internal reagent but the reverse may be true where the plug is permeable to the entering reagent as, e.g., NH_4OH diffusing into $CoCl_2$.

VI. Influence of Temperature.

The system 20% NH_3 diffusing into 2N $CoCl_2$ in gelatin at 24, 15, 7 and 3 deg. C. At the higher temperatures the march of the entering reagent is most rapid and the periodicity appears earliest and the rings are narrower and more numerous. At the lowest temperature no bands at all were formed. The solution of the plug took place most rapidly at the highest temperature. The first suggestion which occurred to us was that these differences are due to differences in viscosity of the medium due to difference in temperature, but we already have shown that a difference in viscosity of the gel has no effect on the diffusion rate. We must therefore explain the difference observed as due to the effect of temperature on the reaction velocity. The reaction velocity of some reactions is high at high temperature and low at low temperature, while in others the reverse is true. The absence of periodicity at the lower temperature may be accounted for as follows. At these temperatures (3 deg. C) reactions take place which do not take place at the higher temperatures, and the resulting products may prevent the periodic precipitation of the $Co(OH)_2$ for at these low temperatures large pink crystals of $(Co(NH_3)_6)Cl_2$ are developed in the upper portion of the tubes (Fig. 92).

VII. *Influence of Light.*

It is well known in the case of photochemical reactions exposure to light at periodic intervals will induce a pseudo-periodicity. There are, however, cases in which the periodicity occurs in the dark. Exposure to light can however induce the onset of periodicity or cause some disturbance in periodicity already established. Such an example is found in the system .25N $HgCl_2$ diffusing into .1N to .003N KI in gelatin. On exposing a tube of internal reagent of such concentration in which no evident periodicity had occurred to the illumination used for photography, banding was at once induced and continued afterward in the dark. In other concentrations (.1N) fine banding had already occurred but on exposure to light there was an evident disturbance of the process in the incidence of broader bands (Fig. 97).

In the system .5N $Pb(NO_3)_2$ diffusing into .1 to .0031N K_2CrO_4 in agar we found that in tubes in which no periodicity was visible (concentrations .0125N and .0062N) exposure to light while we were making a photograph induced periodicity. In some cases it continued after that. Hatchek (1921) also observed that the periodic precipitation of lead chromate is affected by light.

Such variations in banding as observed by Dunin and Schemjakin (1926), to which they appear to have attached considerable importance, can easily occur, as Dogadkin (1928) showed, as the result of external influence, and as we also have found. Their illustration itself shows at once that there was but a single system of red bands and the disturbance in these may have been due wholly to disturbance in the phosphate rings, as we regard them. We have observed such irregularities to occur in this and other systems.

We see, therefore, that in cases in which the equilibrium is easily disturbed, exposure to light can induce true periodicity, or can disturb periodicity already established.

VIII. *Influence of Foreign Ions:*

Influence of the reaction product. The system 20% NH_4OH diffusing into 2N $CoCl_2$ in gelatin plus 2N, 1.5, .5, .25, .1, .05N NH_4Cl, and control. We observed the following:

a. In the two lowest concentrations and in the control the periodicity was normal but disturbances were more and more apparent as the concentration of the reaction product increased. These disturbances were initiated in the final by the accumulation of crystals of $(Co(NH_3)_5)Cl_2$ near the surface, greatest in the highest concentration.

b. The increasingly greater amount of dissolution of the $Co(OH)_2$ at the top of the column and

c. The increasingly greater accumulation of white colloidal precipitate and

d. Less, and in the two highest concentrations, no periodicity.

During the progress of the precipitation however, even in the highest concentrations, there were first laid down (a) a clear zone with crystals, (b) a dark reddish colored zone with no precipitate, and (c) a zone of periodicity alternating blue and white. All these zones grew in depth and by the same token advanced down the tube, the periodicity being lost in a broad white zone.

In high concentrations of NH_4Cl the reagents react in the direction not of $Co(OH)_2$ but of $(Co(NH_3)_6)Cl_2$. For the high concentrations of NH_4Cl other salts may be substituted. If the diffusion rate of NH_4Cl is delayed, as can occur in fine capillary tubes, the $(Co(NH_3)_6)Cl_2$ accumulates and the formation of the blue salt can be obviated entirely. The high concentration of NH_4OH works against formation of the $(Co(HN_3)_6)Cl_2$ and under such conditions merely blue $Co(OH)_2$ is laid down (Figs. 93, 94).

If we reverse the foregoing experiment and add NH_4Cl to NH_4OH which then is allowed to diffuse in to 2N $CoCl_2$ in gelatin we get the same result and we see that the NH_4Cl diffuses readily (Fig. 95).

The idea of the influence of the reaction product on the solubility of the precipitate, thus preventing precipitation until a sufficiently high concentration has been reached, when a new band is formed (in the case of silver nitrate and ammonium chromate), was formulated by Bechhold in 1905 and has been repeated without any theoretical addition by Wo. Ostwald (1925) for the system ammonia diffusing into magnesium chloride.

Our theory postulates the diffusion of the reaction product away from the precipitate to form a complex with the internal reagent, allowing time for the inward diffusion of the entering reagent to meet the complex as it diffuses backward. The two theories are similar in emphasizing the importance of the reaction product but the function of the reaction product is different in them. Bechhold's it merely increases the solubility of the precipitate; in our view it must first unite with the internal reagent to form a complex which then moves backward toward the mouth of the tube to meet the entering reagent which itself has already moved inward some distance beyond the last-formed band.

Influence of various salts (cations). The following chlorides were substituted for NH_4Cl in the preceding experiment, viz. Li, Na, K, Rb, Cs, Ca, Sr and Ba, each in two concentrations, 1N, and .1N, in the gelatin. These salts in low concentrations had no influence. In the higher concentrations the diffusion rate is nearly the same in all. The clear zone is widest in Li $>$K $>$ Rb $>$ Na $>$Ca $>$Ca and was absent from Sr and Ba. The crystals are very prominent in Li, few in Na and are absent from the others. The white precipitate is more abundant in Li >Ca >Na >Cs >Rb >Sr >K >Ba. The blue rings are more abundant in Na >Rb >Cs and absent from the others (Fig. 96). The cations which are most similar in their chemical properties to NH_3 act most like it in the system with which we worked.

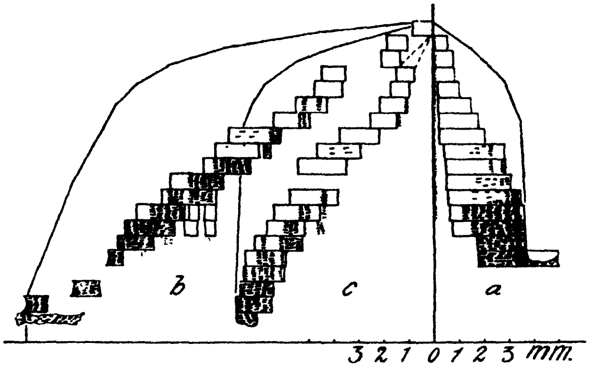
Influence of anions. When $Co(NO_3)_2.6H_2O$ and $CoSO_4.7H_2O$ were added to the gelatin no periodicity was observed. In the higher concentrations of $Co(NO_3)_2$ (2N and 1.5N) the dark red plug is dissolved for some distance from the surface of the gelatin.

Experiments in U-tubes. Recalling Pringsheim's experiments with U-tubes, we have also done a considerable number of similar experiments in order to enable us to see what might be contributed to the solution of the problem of periodicity by means of them. Pringsheim has already found that the precipitate first laid down may move, that is, be dissoved and then recrystallize, and that the column of precipitate may grow first in one direction and later in the other. He observed also the occurrence of periodicity. Our experiments were of value to us in that they enabled us to determine the variety of salts which may occur from the interaction of the two chemical factors in a given system when the one or the other is superabundant. For illustration we may describe the special case of $HgCl_2$ and KI in agar. Experiment: In one arm of a U-tube a saturated solution of $HgCl_2$ and in the other a .25N Ki were put. The tube was made simply by drawing out a tube and bending the wider ends at right angles to the narrow part which was then filled with the medium, agar. The point of meeting of the two reagents was marked on the tube. Here at first a diffuse red precipitate occurred, which persisted for some time but finally disappeared. A new zone of precipitate was soon formed, this time of the yellow salt laid down on the KI side of the primary red zone. The progress of precipitation was observed for 12 days during which (a) a compact column of finely periodic yellow crystals moved slowly forward toward the KI side. This showed also (a) a sort of secondary periodicity consisting in the occurrence of very narrow transverse zones entirely free of precipitate and (b) the laying down of red crystals in the form of rings, paired or grouped, and adsorbed on the glass wall. With time these became more numerous as the column of crystals grew in the direction of the KI. The former periodicity must be regarded as that of crystallization merely, the latter, the red precipitate occurring more and more on the KI, must be due to the periodic higher concentration of this salt. This red salt is strongly adsorbed on the glass wall and occurs as a transverse band only at the end of the column when it ceases to advance.

More complete observations were made with starch as a medium in three U-tubes with the following concentrations:

	$HgCl_2$		KI
a.	saturated solution 0.04	→	0.25N
b.	1/2 do. do.	←	1N
c.	1/4 do. do.	←	0.25N

The arrow indicates the direction of the movement of the crystalline column. In (a) above a permanent narrow zone of fine red crystals was first laid down (text Fig. 3). This was followed by a column of yellow crystals, which showed fine periodicity. For three days only yellow crystals were formed; on the fourth day the red appeared adsorbed on the glass wall in two zones (rings). This red crystallization then spread backward and forward while the yellow disappeared. The red salt became now so abundant as to salt out the medium. (a, text Fig. 3), (b) and (c). The columns moved toward the Hg. The case (b) (text Fig. 3): At the point of meeting only fine yellow crystals were formed. On the second day two narrow rings of red crystals appeared. Subsequently the red crystals became more extensive and the yellow disappeared until on the eleventh day a dense plug of red precipitate was formed and this became irregular in form due to its slight and irregular permeability. It acted as Traube membrane. The history of (c) was similar, but the column did not move so far in the same time. The initial precipitate was, however, of mixed red and yellow crystals.



TEXT FIG. 3

HgCl₂ and KI diffusing into each other. The blank rectangles indicate yellow salt. The appearance of red salt is indicated by short transverse lines. Dissolution of these by stippling. The curves are constructed on an x-y coördinate; but the advance and changes in the columns of precipitate are represented in true but irregular sequence as regards time. A zone blackened by exposure to light is indicated in (a).

Conclusion. Both precipitates are soluble in excess of KI and are laid down only at suitable concentrations. Pringsheim believed that in U-tube experiments the movement of the precipitate always is toward the hypotonic member of the system. This is Pringsheim's rule. In our experiments we found this not to hold in the case of $HgCl_2$ and KI. The movement of the column of crystals in (a) is opposite to that of the osmotic pressure, in (b) and (c), in the same direction and proportional to the difference in concentrations. This movement is not due to non-permeability, since the crystalline zones formed initially and afterwards are freely permeable. Only at the end of the process does an impermeable plug of red salt appear. This always arises from degrading yellow salt and is blackened in strong light but not in the longer wave lengths, viz. to the end of the green. Whether the column move toward the KI or to the $HgCl_2$ side the older part of the column is dissolved and since the salt is not soluble in $HgCl_2$ we must suppose that KCl, the other reaction product, is responsible for the dissolution of the rear end of the column. During the reaction $K_2HgI_2Cl_2$ is formed, which diffuses in both directions. On the KI side the complex is split, yielding HgI_2, and on the $HgCl_2$ side it remains in solution. This we regard as important to account for the movement of the precipitate and for the presence of spaces between bands expressing periodicity (Figs. 98, 99 and text Fig. 3).

X. *Diffusion, and the Head of the Diffusion Column.*

The most satisfactory theory assuming one-way diffusion is that of W. M. Fischer (1925) who followed the theory of W. Ostwald, adding the conception of an induction period which is needed for the separation of one ring from another. He says (p. 326), "Massgebend für die Entstehung der Schichten ist eine bestimmte Diffusionsgeschwindigkeit und zwar eine solche, dass sich die Induktionsperioden der Fällungen ausbilden können. Ist die Diffusionsgeschwindigkeit zu gross, so wird der ausfallende Stoff bei Uebersättigungen gefällt wo keine Unstetigkeit der Ausfällung vorhanden ist, und wir erhalten eine kontinuierliche Fällung."

Our observations support the idea, inasmuch as when diffusion takes place very quickly no rings are formed. Fischer says that the reaction period of barium sulphate is not sufficiently great in water solutions and that he has obtained rings of barium sulphate in such cases in which he introduced some gelatin and dyes, which substances are supposed to lengthen the induction period. We have, however, produced the rings in pure water solutions.

Theory. We see no essential difference between the theories of W. Ostwald and W. M. Fischer. That of the latter has the advantage of greater clearness by virtue of the introduction of the term "induction period," but unfortunately the idea is difficult of experimental proof. The two theories stand or fall together.

Doyle and Ryan have investigated this matter, giving data which correspond to our own, and properly conclude that "Any theory of periodic precipitation which postulates the formation of the precipitates at the head of the diffusion column cannot offer a correct explanation of the phenomenon." Jablczynski's (1926) statement descriptive of the fact is to the effect that though the bands occur behind the head of the diffusion column there is a roughly approximately constant relation between the advance of the reagent and the formation of the bands, in a particular case. The theories which assume that the periodic precipitation takes place at the head of the diffusion column may be at once thrown out of court.

In his conclusion Fricke (1923) says that the diffusion follows the Fick diffusion equation, with which we agree, but we must add that Jablczynski has arrived at quite exact mathematical expressions of the whole phenomenon. In 1903, however, Morse and Pierce had found that diffusion in capillary tubes during periodic precipitation follows Fick's law.

In the case of 10% NH_4OH into 5% $Co(NO_3)_2$ in gelatin, we were able to see that the head of the diffusion column of the entering reaction is some distance in advance of the last periodic band of precipitate. This was due to the alteration of the index of refraction of the gelatin as the NHOH penetrated and caused swelling, so that with suitable illumination we were able to photograph the plane separating the swollen and unswollen gelatin (Figs. 87, 88). It is clear that a reaction must take place in the medium beyond the position of the last ring or, in other words, the position of the band is not the position of the primary reaction. That this is the case is attested by the change in color or other appearance of the medium between the last ring and the end of the diffusion column. It is clear also that the reaction product is free to diffuse both backward and forward.

The head of the diffusion column is to be seen also in the system $AgNO_3$ diffusing into Na_2CO_3 in gelatin. (Fig. 100).

In the system .5N, .5N .25N Pb $(NO_3)_2$ diffusing into .5N, 0.5N into .25N and .25N into .25 N NaCl we observed that at higher concentrations a strong cloud of colloidal precipitate formed behind the head of the diffusion. As a periodic precipitate in the form of pearly spherical globoids appeared the cloudy precipitate disappeared, partly by diffusion forward but chiefly by diffusion backward against the primary diffusion current to contribute to the formation of the crystals (Figs. 101, 102).

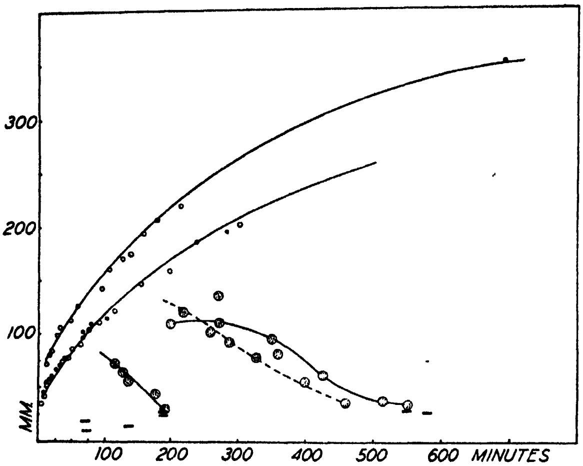
It should be noticed that there was sufficient cloudy precipitate to form only one globoid in one of the cases which we have used for illustration (Fig. 101 d).

In the system .5N $Pb(NO_3)_2$ diffusing into .05N to .0031N NaCl in gelatin again the reaction product appears as a white cloud in advance of the periodic system precipitate. This cloud is itself periodic and gives rise to a periodic grouping of crystalline globoids toward which the cloudy precipitate moves forward, but chiefly backward (Figs. 105, 106).

An excellent example of the backward diffusion of the reaction product was seen in the system .2N Na_2HPO_4 into .5 to 0.16N $CaCl_2$ in test tubes in which the internal reagent was invaded by fungi. These formed small spherical colonies which interfered with the direction of diffusion in such a way that the disc was deformed (Figs. 42, 43, 45). It would be impossible to explain these curious forms except on the assumption of a backward diffusing substance, in this case $NaCl.CaCl_2$.

The system 2% $Pb(NO_3)_2$ diffusing into 4% KI in 6% gelatin supplies us with the best illustration we know of to demonstrate the backward diffusion of the reaction product. For this reason we made a motion picture record on standard size film, the pictures being spaced four minutes apart. In this case, the like of which rarely occurs, the reaction product occurs in an exceedingly fine colloidal cloud in which, due to the smallness of the particles, there is no hindrance to diffusion (Figs. 114-115).

The final form of the periodic precipitate is a banding of white precipitate which is oxyiodide of lead, but the primary reaction product which is formed far in advance is the yellow oxide PbI_2. When we plot the course of advance of the yellow cloud from data obtained by measuring the photographic images, we obtain a curve, the shape of which is that of a diffusion curve. (Text fig. 4). For two cases we obtained quite the same values. In both curves, however, there occur certain deviations which indicate that the diffusion occurs periodically and these deviations are to be found at the time when we observe the impact of the curve of the backward diffusing cloud.



TEXT FIG. 4

Plotted from measurements of a motion picture, a few frames of which are shown in Figs. 114, 115. Large stippled circles represent the clouds of backward-moving complex. Short horizontal lines represent periodic bands. Upper two curves, the advancing heads of two columns.

Under observation we can see the formation of a brilliant cloud at the forward end of the diffusion column which at length begins to move backward to the outer end of the column and there disappears, but *at precisely this time a band of precipitate is formed.* We have plotted the movement of two such clouds in the accompanying diagram and in spite of obvious difficulties of measurement there is no doubt of the general correctness of the data. We observe that the first cloud moved more quickly than the second, but both were observed to end in the formation of the ring. It is evident that if the whole story were similarly plotted we should have a cloud for each band formed, but that each earlier cloud would be represented by a steeper curve than that of the next following.

If the white periodic precipitate is laid down in this way we must believe that the yellow precipitate is laid down in similar fashion. We must further infer that the yellow product here is $KI.PbI_2$ which diffuses backward against the higher concentration of the entering reagent. At the point where both will be sufficiently concentrated a colloidal precipitate will occur. The above mentioned relations are represented diagrammatically in text Fig. 5.

XI. Adsorption.

In the system 1.25 N $AgNO_3$ diffusing into .1 to .0062N $K_2Cr_2O_5$ in gelatin the following takes place. First, there is a periodic precipitation of Ag-phosphate in fine white bands. On this a red silver chromate (a basic complex) is strongly adsorbed periodically. If the process is followed microscopically the gradual darkening of the particles constituting the Ag-phosphate bands can be easily and surely followed. In the interspaces there will be a lower concentration of the entering reagent and here the yellow salt appears so that in time the white phosphate rings not already darkened become yellow since adsorption here occurs also.

The periodicity of the Ag-salt appears to be exactly parallel to that of the phosphate, or harmonic with it, since the identity of the Ag bands (at first sets of discrete rings) with the phosphate bands is at first quite evident. As the precipitation column lengthens, however, and the phosphate bands sepaarate, and become irregular, or may even fail to form, the Ag bands then become displaced or vague, consisting of clouds or scattered granules, a condition typical of this system in agar. We must infer, therefore, that the apparent harmonical relation is due to the very strong adsorption of the Ag salt on the phosphate. The phosphate salt is in its turn adsorbed on the glass wall and the earliest deposition of the red salt is always where the phosphate is strongly adsorbed on the glass wall and hence we may obtain groups of red rings (Figs. 74, 75, 76a, 79, 103, 104).

Experiments with chromates are very difficult to explain chemically because the salts are complex and not well understood. We know merely that the yellow salt is the chromate and that the red salts are different intermediate stages between the complexes of the basic salt of the metal and the chromate. These complexes will have different electrical charges and different surface properties and therefore we cannot be surprised if we find different adsorption relations among these salts. And, as we have already found that the periodicity is induced largely by the adsorption relations among these salts, we have met with different periodicities in the same system with different kinds of chromates since their adsorption relations are different.

Concerning the system silver dichromate-gelatin, Hedges raises the question as to the nature of the "pale yellow fringe," this according to Friend being silver chromate and Reinhard sodium chloride. But Hedges got the same results even after the supposed chlorides had been precipitated by the addition of silver nitrate and further that the addition of a drop of silver nitrate to the yellow fringe induced an independent ring system. He regards the first product of the reaction to be silver dichromate which is afterwards coagulated into rings in excess of the indiffusing silver nitrate. But we have shown that clear cut rings occur by adsorption of the reaction product on rings already present, viz. phosphate rings (Morse and Pierce, 1903). We have also learned that the silver chloride banding has a different periodicity from that of the supposed silver chromate system, even in the presence of sodium chloride. The silver dichromate appears to be negatively adsorbed on silver chloride but positively adsorbed on phosphate. We would also say that the yellow fringe contains chromate and a complex of chromate and KNO_3.

Here we quote P. B. Ganguly (1927) as pertinent. It is well known that the charge on a colloid particle can be traced in many cases to the presence of adsorbed ions. In certain cases by the introduction of suitable ions the sign of the charge can be changed at will. Lottermoser obtained silver halide solutions which were positively or negatively charged according as an excess of silver salts or of halide salts was used. Thus the sign of the charge was directly dependent on the nature of the common ion which was present in excess and was capable of being adsorbed by the precipitate.

XII. Recrystallization and Chemical Transformations.

In the system $K_2Cr_2O_7$ diffusing into $AgNO_3$ in gelatin we have observed that the character of the salt formed depends on the concentration of the entering reagent. At first when the concentration of the entering reagent is low and the Ag salt is excess, only a red salt is formed, and as the concentration of the K salt increases with further diffusion the red salt disappears and recrystallizes as a yellow salt at some distance away, the red salt evaporating and condensing as yellow and partly recrystallizing *in situ.* Thus is given rise to a very complicated pattern (Figs. 107, 108). In the inverse case ($AgNO_3$ into $K_2Cr_2O_7$ in gelatin) at the mouth of the tube the salt formed is red, the yellow salts appearing further in the tube where the concentration of K salts is higher; and in the gelatin, since the yellow salt is adsorbed on the phosphate it is sharply periodic.

But if agar is used as a medium (Ag diffusing into K) the yellow salt is not sharply if at all periodic, while the red salt is periodic, sometimes regularly, sometimes irregularly. Since the red salt is adsorbed on the yellow and since the nuclei formed are irregular in size, there is a transformation of the red salt from a finely colloidal to a coarsely crystalline condition (Fig. 109). Inverted, (viz. K diffusing into Ag in agar) the advancing zone is marked by disappearance of the darkish brown color in the medium (reduction of silver) indicating the head of the diffusion column. Near to the point of entrance there appears a dark membranous colloidal precipitate in rounded or irregular (comet-shaped) masses with vague, if any, periodicity accompanied in higher concentrations by beautiful red crystals. The advance of high concentration of the entering reagent is accompanied by chemical change of the dark red to a pale (white?) precipitate, also with vague periodicity. At low concentrations of the internal reagent, the time factor becomes such that the red salt is wholly adsorbed on the glass wall (very like Figs. 60, 61).

When starch is the medium (K diffusing into Ag), coarse dark red irregular crystalline masses with metallic lustre appear. These are semi-permeable (Traube) membranes which grow into curious forms (see above). As the entering reagent increases in concentration the dark red salt disappears and is in part recrystallized *in situ*, producing pseudomorphs of the original precipitate, and in part is sublimated and deposited elsewhere (Figs. 60-64).

The inverse (Ag diffusing into K) appears to be negative, the red salt appearing at once, and no change occurs.

In $Pb(NO_3)_2$ into $K_2Cr_2O_7$ in gelatin we find the same general conditions resulting as in the case of the Ag corresponding system, since these chromates make quite analogous chemical complexes. Here no phosphate rings occur and the chromates are positively adsorbed on the glass wall. Since we get two systems of periodicity, one near the mouth of the tube and the other deeply removed therefrom, we must infer that we are dealing with two different chromates. In the case of higher concentrations two different sets of bands are laid down simultaneously (Fig. 111 a and b).

In the system $HgCl_2$ into KI in gelatin, the precipitate is laid down as fine red crystals which give way deeper in the tube to yellow where the KI is in excess. In both gelatin and starch there are always two modifications of the salt, yellow and red, and these may be laid down periodically. The red precipitate occurs where the Hg concentration is higher (Figs. 27, 28, 29).

In the system $Pb(NO_3)_2$ into KI in gelatin the primary precipitate occurs as a yellow salt in a finely dispersed colloidal state. As the concentration of $Pb(NO_3)_2$ increases, the yellow salt PbI_2 is changed into a basic lead iodide. We have already described the process above.

At low concentrations of KI only white bands are formed, i.e., when $Pb(NO_3)_2$ is in high excess. If the concentrations are nearly the same or if KI is in excess, the yellow precipitate is laid down to be changed to white as the concentration of the $Pb(NO_3)_2$ increases (Figs. 114, 115).

In the systems $(NH_4)_2HPO_4$ into $CaCl_2$ and Na_2HPO_4 into $CaCl_2$ at high concentrations of the internal reagent, at first crystalline spheroids are formed with little if any periodicity. At the same time white rings and discs appear. With time the crystals disappear and are recrystallized as material added to the rings. In low concentrations only rings and discs appear and no crystals. (Figs. 67, 68, 83, 84).

When $Pb(NO_3)_2$ diffuses into NaCl in water a fine colloidal precipitate is first formed which quickly condenses by evaporation and recrystallization into relatively large crystals (Fig. 110). In gelatin crystals appear only in the form of spheroids.

XIII. Density of the Initial Precipitate (plug) and its Permeability.

According to Bradford the interaction of an aqueous reagent on a gel containing a suitable solute will create a solid boundary surface between them and thus initiate periodicity. This however is only a special case and we have found that when the initial precipitate is discontinuous it is equally possible to obtain periodic precipitation.

It is generally to be observed in almost all, if not all, systems that the higher the concentration of the interacting reagent the slower the diffusion of the entering reagent and the slower therefore the growth of the precipitation column. The slower the diffusion also the closer together are the periodic bands and the more regular the form of the precipitate laid down. (Fig. 74 *etc.*).

XIV. Absence of Periodicity, Apparent and Real.

We have already committed ourselves to the view that the problem of periodicity involves also the problem of non-periodicity. Not seldom in the literature authors express the opinion that one medium or another is not "good" for the production of periodic precipitation. We have in the same breath to explain the absence as well as the presence of periodicity. That purer gels are less suitable for the production of rings because of the absence of salts, as suggested by Doyle and Ryan (1929), is well known, but we have shown that the difference can be explained by adsorption.

Fischer and McLaughlin (1922) say that periodic precipitation is possible only in those cases where a semi-permeable membrane is formed, which later becomes permeable. We have found that it can occur without such a membrane, as in the cases where only widely separated crystals constitute the initial precipitation and where only rings on the glass wall are formed accompanied or not by discs, which in any event only partially block the path. The same can be said of the theory of Traube and Takehara (1924). The non-appearance of periodicity or the inappreciable character of it may not actually correspond to the objective fact.

We have seen many cases where a very slight amount of periodicity, quite evident to the eye, might lead to the conviction that everywhere else periodicity is present but inappreciable to the senses. And also in the same concentrations of reagents and under precisely similar, or even identical, conditions periodicity occurs in one tube and not in another, or in one part of a tube and not in another. (Fig. 20). We are therefore led to predicate non-periodicity as the logical continuum of periodicity. We believe we are right in regarding certain cases as non-periodic.

Case. $Ag(NO_3)_2$ into $K_2Cr_2O_7$ in starch. In six tubes coarse crystalline precipitate occurred non-periodically, except in a region in one of them where the crystals were smaller, where distinct banding occurred (Fig. 20).

Case. 2% $CaCl_2$ into ammonium oxalate and inverse. In the former a uniformly distributed precipitate of plaque-shaped crystals without periodicity (Figs. 72, 54, 55).

Apparent absence of periodicity may, on microscopic examination, turn out not to be objectively non-periodic (Stansfield, 1917). Case. $Pb(NO_3)_2$ diffusing into $K_2Cr_2O_7$ in gelatin in tubes 3 millimeteres in diameter revealed no periodicity to the eye, even with a strong lens. On examining with a microscope a section from the surface at the open end of the tube we found a sharply defined very fine periodicity (Fig. 112). Much the same was seen in $HgCl_2$ into KI in agar. In gelatin no periodicity was observed (Figs. 29, 30). Case. $K_2Cr_2O_7$ into $Pb(NO_3)_2$ in agar in capillary tubes. No concentration showed any visible periodicity. Nevertheless when we examined all the tubes microscopically we found a very fine periodic banding in two concentrations (.05N and .025N) (Fig. 113).

We are convinced that many observers who have failed to find periodicity have done so because they have merely failed to see it. Case. $Pb(NO_3)_2$ into

$K_2Cr_2O_7$ in agar. At concentrations .5N into .0062N. One tube of a set of six tubes was accidentally plugged by an air bubble which effectively lowered the diffusion rate of the entering reagent. For a short space beyond the bubble the precipitation was uniform but at a certain point it changed abruptly into a distinctly periodic condition. In all the other tubes periodicity did not begin for a long time later (Fig. 57). In such cases we have critical conditions in which a slight difference of any factors which influence periodicity in one way or another many hinder or effect it.

XV. Inversion of the Reaction.

Cases (a) $CaCl_2$ diffusing into ammonium oxalate and (b) its inverse. In case (a) we obtained a very fine colloidal precipitate, but no periodicity in either case. (Figs. 116, 117).

Cases (a) NH_4OH diffusing into $MgCl_2$ in gelatin and (b) its inverse. In one case (a) we obtained periodicity, in the other (b) little or no periodicity,[1] in test tubes. In capillary tubes we obtained periodicity in both cases—another proof that at critical points slight differences may determine the incidence of periodicity (Figs. 1-4).

Cases (a) $AgNO_3$ diffusing into K_2CrO_4 in gelatin and (b) its inverse. Periodicity occurred in both cases but in one case (b) there were no phosphate rings and the precipitate was very strongly adsorbed on the glass wall, while in case (a) phosphate rings occurred and the Ag-chromate was adsorbed on the Ag-phosphate precipitate, never on the glass wall. We therefore see that in the two cases the properties of the medium are different (Figs. 7.6a, 77). We have observed similar differences in many cases. If we change the salt in the gelatin we may get a medium with opposite (electrolyte) properties with respect to the precipitate.

Bradford states his belief that the occurrence or non-occurrence of bands of the same substance in different gels is due to the influence of the reaction medium on the dispersity of the precipitate. But we think it is due to the adsorption relations between the precipitate and the gel or the glass wall.

Fricke (1923) very pertinently remarks that the various factors of adsorption, coagulation of electrolytes, influence of solubility of the precipitate, etc. regarded as fundamental by other authors, are not so, but on the contrary are not essential—"wesentlich." The gel as a medium has, according to him, the chief rôle of furnishing a steady diffusion current and prevents convection streams.

Discussion

In the large majority of cases which have been studied periodicity occurs. In exceptional cases it does not occur. We shall endeavor first to formulate a theory to account for periodicity.

In the practice of inorganic chemistry the reactions which are allowed to take place do so in a pure medium, pure water for the most part, a medium which is continuous and presents no complications, such as surface phenomena. Biological reactions and those in which we meet with periodicity are quite different systems. First, they take place under circumstances where there are great mixtures of substances. Second, these take place in a medium which has viscosity and high concentrations and where the diffusion of reagents and reaction products proceeds very slowly as compared with that in a watery or gaseous medium. Third, they take place on microstructures, in capillary spaces characterized by the presence of many interfaces where physical forces complicate the chemical reactions. From these three considerations we get divergencies in the solubility of the precipitates e.g., we obtain crystalline modifications which we never get in a watery medium at corresponding concentrations of the precipitate. Further, we get different dimensions of crystals ranging from the finest colloidal suspension to the coarsest crystalline or spherocrystalline product. And still again, the time factor is sufficiently long for reactions to take place for which normally there is insufficient time.

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[1] As pointed out above, in a repeat of these experiments we obtained a clear cut band in one concentration. (Fig. 2a Plate IX.)

We must also take account of the fact that surfaces in capillary spaces, e.g. in fine capillary tubes, between sheets of glass, etc., can act so strongly by way of adsorption that the intermolecular forces are more or less overcome or nullified. In those cases where a soluble reaction product remains in the vicinity of the place of reaction such a high concentration may occur that in many cases complex salts are formed.

We would suppose that every biological reaction should be periodic, since in the great majority of cases in our experiment we procured periodicity; but we must not overlook the important fact that the systems in which we obtain periodicity are such in which diffusion streams move along a single path in a single direction or the reverse, whereas in biological materials the diffusion currents may, and probably do, move in all directions, or at least in many, certainly very rarely in one direction alone. We admit that it is quite thinkable that the conditions for unidirectional diffusion may be supplied in some cases, as suggested, for example, by the transverse striping in some elongate plant leaves. Even the stripes of the zebra, a favorite example, might conceivably result from unidirectional diffusion of pigment or pigment-forming substance in the ectoderm of the blastodisc but, on the other hand, nobody yet knows that this is the case. Again, we can obtain periodical precipitation in plant structures (Lloyd and Moravek, Rouppert) but no one can say when transverse markings are met with, either in leaves or trichomes, etc., in nature that they are actually produced in this way. It is our opinion quite idle to cite the annual rings of trees, in the roots, etc. of plants (Beta, etc.) and many other oft-quoted examples, and we dismiss such loose analogies at once from consideration. The much argued case of agate may be in better case.

In a system in which a periodic precipitate may occur, a first membrane must be laid down. In this membrane two kinds of ions are precipitated and at the same moment there must be close to the membrane a very high concentration of the reaction product, which now diffuses in both directions. (It at the same time increases the osmotic value of the medium, and this may therefore swell.) That part of the reaction product which diffuses toward the internal reagent causes, when the concentration becomes high enough, the formation of a complex salt.

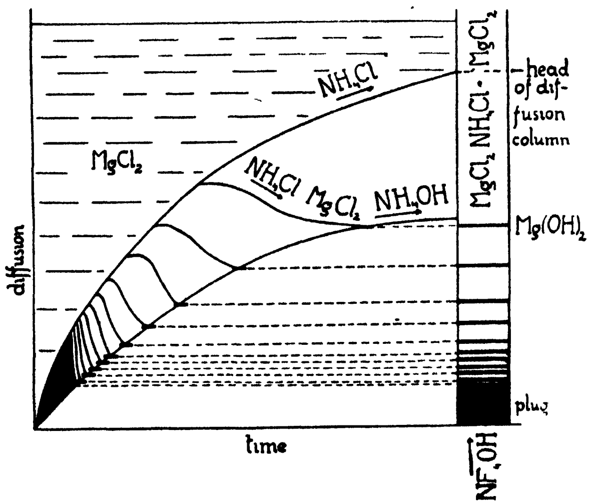
The space in the diffusion column expressed as the difference between the curves of the diffusion head and ring formation carefully worked out by Jablczynski (1926) for a number of systems is the space in which the complex which we postulate is formed and in which it diffuses toward and to meet the entering reagent. (text Fig. 2).

It will be apparent that various factors, essentially of secondary importance (adsorption, concentration and nature of medium, nature of reacting salts, viscosity, influence of foreign ions, etc.), may in special cases play so large a part that the essential factor, the backward diffusion of the complex, may be obscured and therefore we meet with theories which appear to explain special cases but which fail when they are applied to the entire known series of cases. Such complexes are frequent and well known in the field of inorganic chemistry, but sometimes are not known and we must suppose that the medium (respectively the surfaces) permit such to occur. When there has been reached a sufficiently high concentration of the reaction product for the formation of such a complex with the internal reagent to be achieved, the latter (the internal reagent) will diffuse toward it from both directions. Having once formed, the complex itself will begin to diffuse in both directions. In the meantime the ion of the entering salt which forms the insoluble precipitate diffuses through the initial membrane or plug, but meets with none or, at any rate, a much reduced number of ions of the internal reagent with which it reacts and therefore must move some distance before it meets that part of the complex which is diffusing backwards. It reacts also with more or less of the internal reagent on its way and in this matter also arises more or less precipitate in the interspace, which is rarely quite free from such.

When the complex and the primary reacting entering ion meet, oversaturation will then occur and precipitation will begin. If in the special case of tubes, etc. the product is adsorbed on the glass wall, a sharp ring will be formed, followed by a disc which is always somewhat further in the tube than its corresponding ring. The saturn structure is thus accounted for. If the product is not adsorbed on the glass wall a more or less diffuse band occurs. Irregularities consisting of interruptions in bands on the glass wall, producing sometimes spirals, sometimes other irregularities, are all caused by chance interruptions in diffusion. We know positively that a small bubble can cause the appearance of spirals in place of circular bands.

Each time this occurs the reacting ions of the internal reagent will be diluted more and more and the external reagent must then diffuse further and further in order to meet concentrations suitable for precipitation and hence the bands will be formed at increasing distances. The complex may be colorless or colored, or it may be an invisible or a visible colloidal cloud. In the case of $Pb(NO_3)_2$ diffusing into KI in gelatin we have an example of the last. It is evident that the above process demands suitable relative concentrations of both of the entering ions. If the difference of concentration is too small the two ions will move through the plug or initial membrane at approximately equal rates and a continuous precipitate will be formed. If there is a large difference of concentration of the entering ions periodic precipitation will occur. Such a difference occurs when one ion is used up in the reaction, setting the other free. The difference in concentration of the entering ions will be greater the lower the concentration of the entering reagent and the sooner will periodicity occur. (Text Fig. 5).

We have been led to formulate the foregoing theory from our actual observation of cases in which a movement backward of precipitate to form a ring-and-disc could be observed and such backward movement we regard as an incontrovertible fact. Precisely what complexes will occur in any particular case is of secondary importance. (Figs. 114, 115, text Fig. 4).



TEXT FIG. 5
Diagrammatic scheme to show the backward diffusion of a complex formed near the head of the diffusion column to form a band of precipitate where the entering reagent is met with.

We are equally of the opinion that in some cases no periodicity occurs. The following conditions are possible:

1. The initial precipitate is permeable to the ion which does not enter into the reaction. If, however, the ion does not react with the internal reagent to form a complex the equilibrium is not disturbed, no backward diffusing substance is formed and no periodicity occurs.

2. The initial precipitate is permeable to both ions, but if these are in too high concentration the ratio of the ions of the entering reagent will be only slightly disturbed for some time dependent on the concentration and the precipitate will be continuous.

3. The initial precipitate, that is the membrane first formed, is not at all, or only very slightly, permeable for the entering ion which does not enter into the reaction. If the former, only a membrane will be formed; if the latter, a column of precipitate is built up without periodicity.

Note: The work reported in this paper was done by the authors jointly in the Botanical Laboratory of McGill University, Montreal, and, in part, in co-operation at Masaryk University, Brno, C.S.R. During the period the junior author was Research Associate of the Department of Botany, McGill University. The senior author spent six weeks in the summer of 1930 at Masaryk University. The expense was partly met by a grant from the Cooper Fund, Medical Faculty, McGill University, for which grateful acknowledgment is here made.

References

H. Bechhold: Z. physik. Chem., **52**, 185, 199 (1905).
S. C. Bradford: Science Progress, **10**, 170-174; Biochem J., **14** (1920).
W. H. Chapin and H. N. Holmes: J. Am. Chem. Soc., **40**, 1187 (1918).
A. C. Chatterji and N. R. Dhar: Kolloid-Z., **31**, 15-19 (1922); **37**, (2-9) 89-97 (1925); **40**, 97-112 (1926).
E. C. H. Davis: J. Am. Chem. Soc., **44**, 2698-2704 (1922).
B. Dogadkin: Kolloid-Z., **45**, 136-140 (1928).
M. S. Dounin and F. M. Schemjakin: Kolloid-Z., **39**, 50-52 (1926); **48**, 167-170 (1929).
Martin H. Fischer and G. D. McLaughlin: Kolloid-Z., **30**, 13-16 (1922).
W. M. Fischer: Z. anorg. Chem., **145**, 311-364 (1925).
R. Fricke: Z. physik. Chem., **107**, 41-64 (1923).
R. Fricke and O. Suwelack: Z. physik. Chem., **124**, 359-393 (1926).
P. B. Ganguly: J. Phys. Chem., **31**, 481-495 (1927).
E. Hatchek: Proc. Roy. Soc., **99A**, 496-502 (1921).
E. S. Hedges and R. V. Henley: J. Chem. Soc., **1928**, 2714-2726.
K. Jablczynski: Kolloid-Z., **40**, 22-28 (1926).
E. Karrer: J. Am. Chem. Soc., **44**, 951 (1922).
K. Lagergren: Svenska. Vet. Akad. Handb., **24**, 2, Nos. 4 & 5 (1899). (through Bradford).
R. E. Liesegang: Z. wiss. Chem., **38**, 1-12 (1914).
F. E. Lloyd: Flora N. F., **18-19**, 371-385 (1925).
F. E. Lloyd and V. Moravek: Plant Physiol., **3**, 101-130 (1928).
A. B. Macallum: Proc. Roy. Soc., **77B**, 165-192 (1906).
H. McGuigan and G. A. Brough: J. Biol. Chem., **58**, 415-423 (1923-24).
H. W. Morse and George W. Pierce: Z. physik. Chem., **40**, 589-607 (1903).
J. N. Mukherjee and A. C. Chatterji: Kolloid-Z., **50**, 147-159 (1930).
K. Notboom: Kolloid-Z., **32**, 247-252 (1923).
Wo. Ostwald: Kolloid-Z., **36**: (Ergänz. Bd.) 380-390 (1925); **40**, 144-148 (1926).
R. B. Peet: "A study of periodic precipitation," (1925). MS. in Stanford University Library.
Katharina Popp: Kolloid-Z., **36**, 208-215 (1925).
N. Pringsheim: Jahrb Wiss. Bot., **28**, 1-38.
K. Rouppert: Bull. Acad. Polon., B. 785-800 (1925) (printed 1926).
K. C. Sen and N. R. Dhar: Kolloid-Z., **34**, 270-279 (1924).
J. Stansfield: Am. J. Sci., 4, **42**, 1-26 (1917).
J. Traube and K. Takehara: Kolloid-Z., **35**, 245-247 (1924).
E. Weitz: Z. angew. Chem., **37**, 391 (1924).
J. Wulff: Z. physik. Chem., **B.6**, 43 (1929).

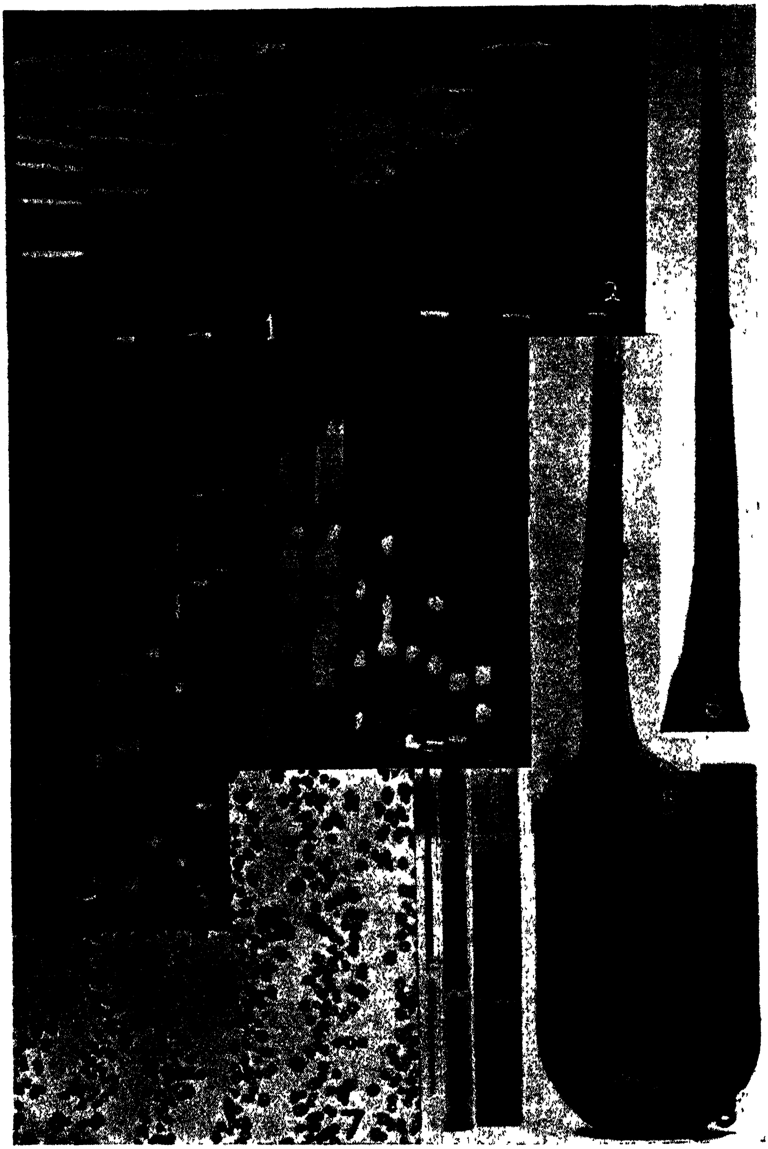


PLATE I

References to the text are given in brackets

1. 12N, (on the left) 6N, 3N and 1.5N NH_4OH diffusing into 1N $MgCl_2$ + 8% gelatin in test tubes. (p. 1512, 1530, 1543)
2. Saturated solution .5, (on the left) .25 and .125 $MgCl_2$ diffusing into 1N NH_4OH in 8% gelatin in test tubes. (p. 1513, 1543)

2a. See plate IX. .5 saturated solution MgCl diffusing into 1N NH_4OH in gelatin. A perfect zone formed. (p. 1513, 1524)

3. Same as (1) above, but in capillary tubes. Entrance to tubes above; highest concentration on the left. (p. 1512, 1530, 1543)
4. Same as (2) above, but in capillary tubes. Entrance to tubes below; highest concentration on the left. (p. 1513, 1543)
5. Trichome of *Begonia* sp. Ammonium sulphide diffusing into cobalt-sodium hexanitrite. (p. 1513)
6. Trichome of *Laportea canadensis* similarly treated. (p 1513)
7. 4% KI diffusing into 1% $Pb(NO_3)_2$ in a capillary space between glass plates. (p. 1513, 1516)
8. Effect of difference in diameter of the glass tubes, viz. 1, 3, 10 and 50 millimeters. 20% NH_3 diffusing into 2N $CoCl_2$ in 10% gelatin. (p. 1513)

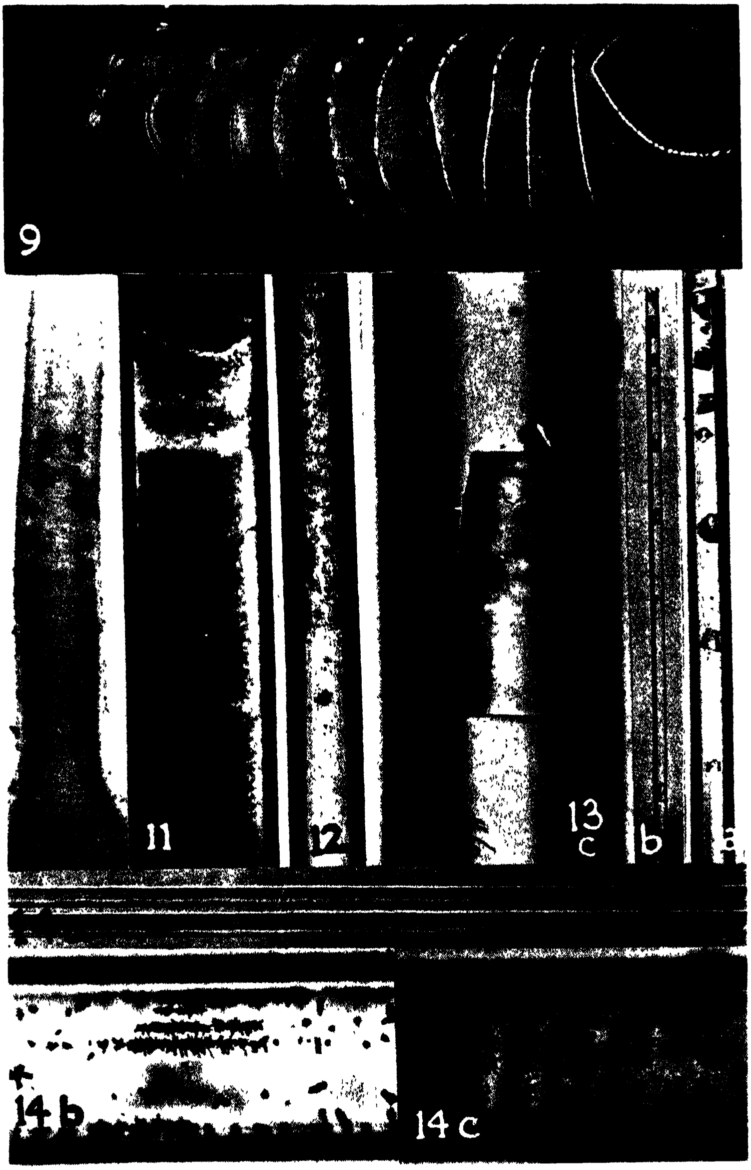


PLATE II

9 .2N $Pb(NO_3)_2$ diffusing into 1N $K_2Cr_2O_7$ in a very thin capillary space (p 1513)

10 Trichome of *Begonia* sp as in fig 5 (p 1513)

11 HCl (gas) diffusing into NH_4OH (gas) in capillary tube (p 1515)

12 NH_4OH (gas) diffusing into HCl (gas) in capillary tube (p 1515)

13 HCl (concentrated) diffusing into 30% NaCl in capillary tube (a) earlier, (b) later, (c) a single crystal. Tube 17 millimeter in diameter (p 1516)

14 Na_2CO_3 diffusing into 25N $AgNO_3$ in H_2O; capillary tube 2 mm. in diameter (a) final condition, (b) detail of (a), (c) early rings (p 1516, 1519)

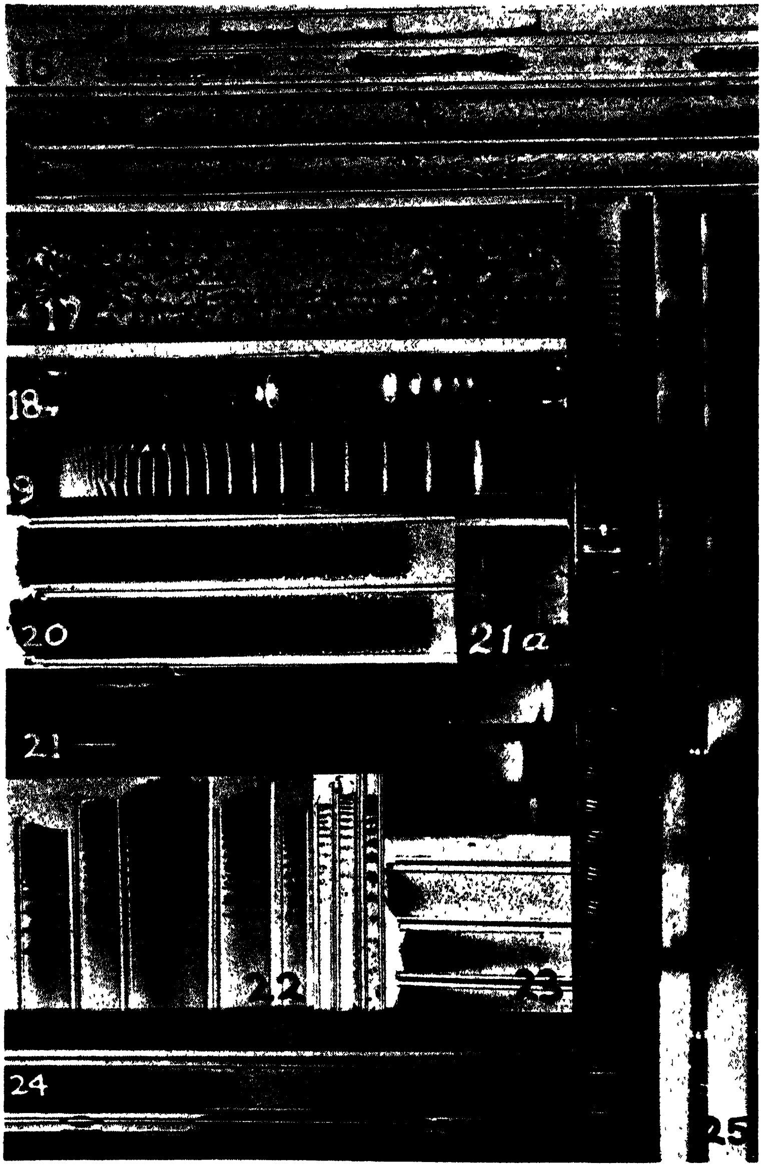


PLATE III

15. 1N NaCl diffusing into 1N $AgNO_3$ in capillary tube .3 millimeter in diameter (p 1516, 1524)
16. 1N $BaCl_2$ diffusing into 1N K_2SO_4 in capillary tubes .3 millimeter in diameter. (p 1516)
17. Detail of fig. 16, showing two zones (p. 1516, 1524)
18. .25N $Pb(NO_3)_2$ diffusing into 1N KI in starch (p 1517)
19. The same as fig. 18, but in agar (p 1517, 1523)
20. $AgNO_3$ diffusing into $K_2Cr_2O_7$ in starch (p 1517, 1542)
21. The same as in figs 18 and 22, but in gelatin Column yellow, discs white (p 1517)
21a. The same A single band showing the white colloidal precipitate imbedded in a vitreous mass. (p 1517)
22. The same as fig. 18. The five left hand tubes, corn starch paste, the three right, potato starch. (p. 1516-7, 1523)
23. .5N $Pb(NO_3)_2$ diffusing into .0062 $K_2Cr_2O_7$, in starch (above) and agar. (p 1518)
24. .5N K_2CrO_4 diffusing into 1N – 025N $Pb(NO_3)_2$ in starch (p. 1518, 1529)
25. .5N $AgNO_3$ diffusing into 2% $K_2Cr_2O_7$ in gelatin (right) and agar. The dark precipitate is red, the light pale yellow. (p 1517, 1518)

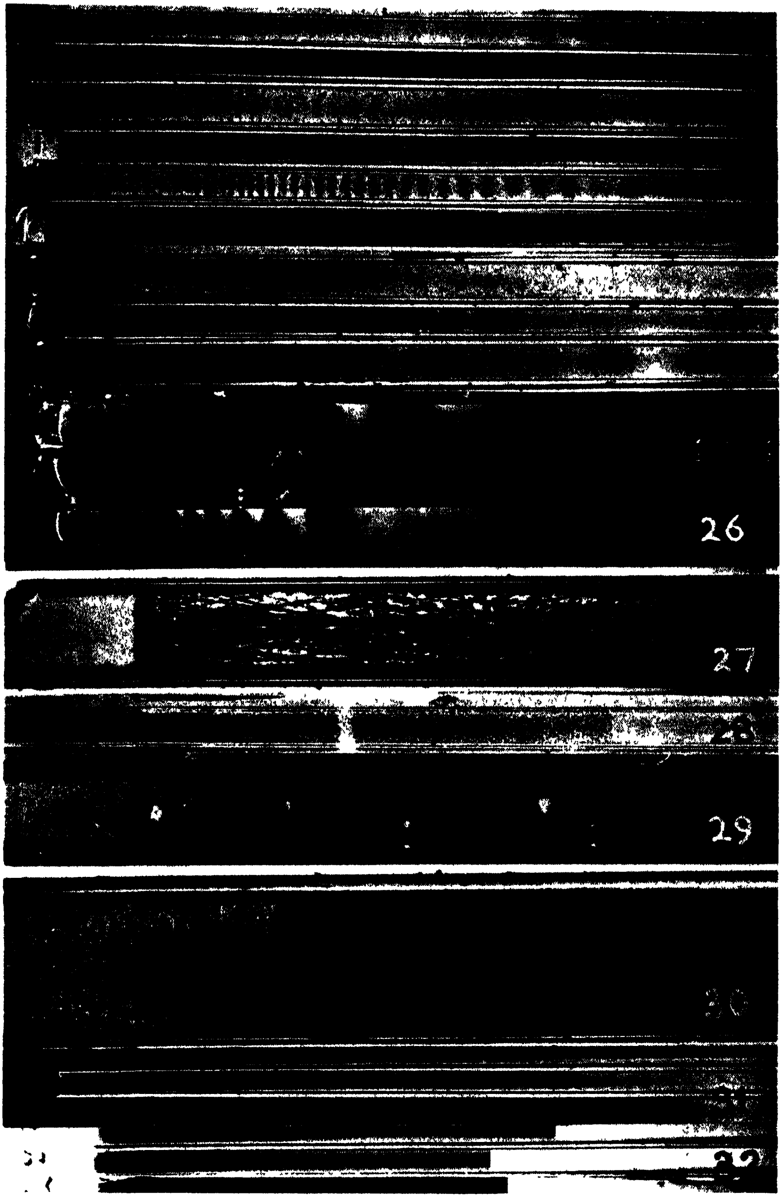


PLATE IV

26 $AgNO_3$ diffusing into 1N-0031N $K_2Cr_2O_7$ in agar (nos 1-11 from bottom) and in starch (nos 2-12). The lowest three tubes were photographed by reflected light, the others by transmitted light (p 1517, 1528)

27. .1 saturated solution $HgCl_2$ diffusing into 1N KI in starch (p 1518, 1541)

28. The same tube, later The pale band across the middle of the tube is an accidental reflection (p 1518, 1541)

29. 25 $HgCl_2$ diffusing into 1N KI in agar. (p 1518, 1541-2)

30. The same as fig 29, but in gelatin (p. 1518, 1542)

31. 5N $Pb(NO_3)_2$ diffusing into 05-.025N K_2CrO_4 in starch (p 1518, 1529)

32. The same as fig 31, but in agar (See also figs 51, 52, 57). (p 1518)

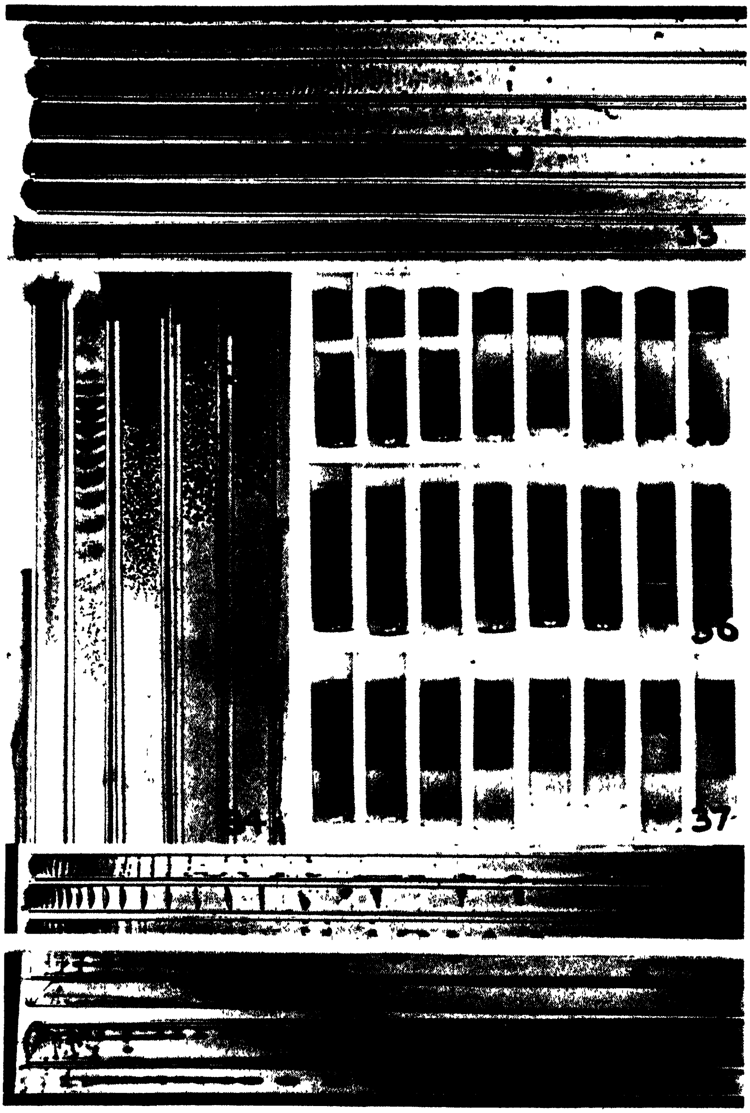


PLATE V

33. .5N $Pb(NO_3)_2$ diffusing into 1N-.0031N K_2CrO_4 in gelatin The highest concentration below (p 1518, 1526, 1528)

34. 25N $Pb(NO_3)_2$ diffusing into .1-.006N $K_2Cr_2O_7$ in gelatin. The highest concentration to the right (p 1518, 1528)

35. 20% NH_4OH diffusing into 2N $CoCl_2$ in 5% gelatin (tubes 1-3 from the left), in 7% gelatin (tubes 4 and 5) and in 15% gelatin (tubes 6-8) Gelatin dissolved at 50°C After nine days (p. 1515, 1518)

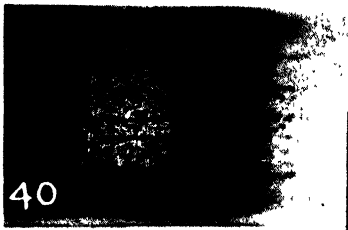
36. As in fig 35 but the gelatin (10%) was heated variously: tubes 1 and 2 (from the left) heated in water bath till dissolved; tubes 3 and 4 as above, but kept at 80°C. for 30 seconds, tubes 5 and 6 kept at 100°C for 30 seconds; tubes 7 and 8 kept at 100°C for two hours Photo after 16 days (p 1518)

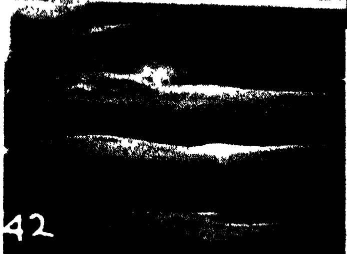
37. As in fig 35, but in various concentrations of gelatin.

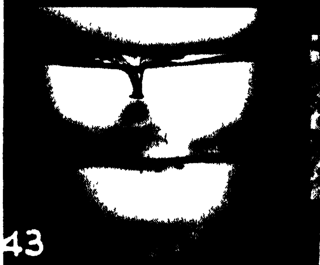
Tube no. 1 (from the left) 15% gelatin
2 12% "
3 11% "
4 10% "
5 9% "
6 7% "
7 5% "
8 3% " (p. 1519)

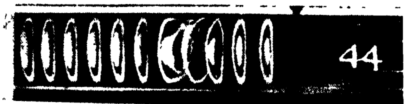
38. .5N K_2CrO_4 diffusing into .025N $AgNO_3$ in gelatin (p 1520)

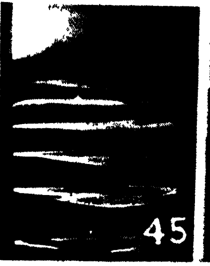
39. The same as fig 38, but .0125N $AgNO_3$ (p. 1520)

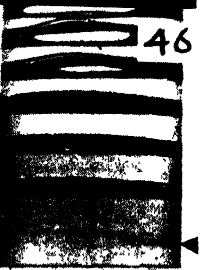


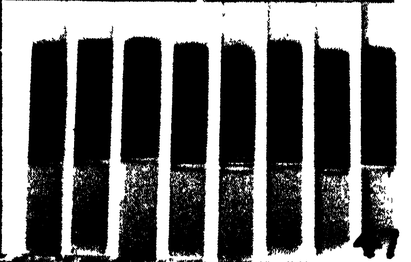


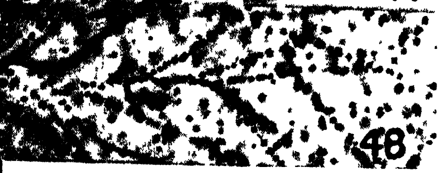


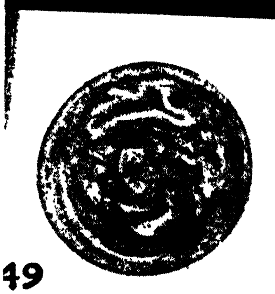












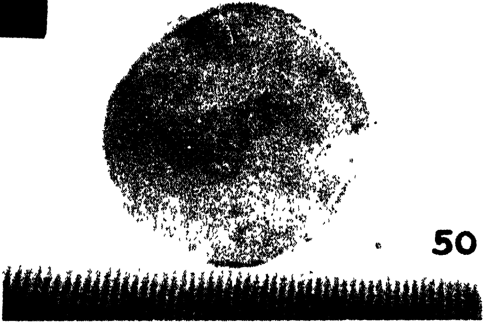


PLATE VI

40 2% $K_2Cr_2O_4$ diffusing into 25N $AgNO_3$ in gelatin (p 1520)
41 The same, at a later stage, to show the disc (p 1520)
42. 2N Na_2HPO_4 diffusing into 0062N $CaCl_2$ in gelatin Reflected light (p 1522, 1537)
43 The same Detail, transmitted light (p 1522, 1537)
44 NH_4OH diffusing into $CoCl_2$ "Saturn structure" The ring is formed on the glass wall earlier than the disc (indicated by the black triangle) (p 1520)
45 The same as fig 42, to show rings on glass wall without discs being formed (p 1520, 1537)
46 NH_4OH diffusing into $CoCl_2$. "Saturn structure" The ring on the glass wall is nearer the mouth of the tube than the disc A new ring is being formed, as in fig 44 (p 1520)
47 20% NH_4OH diffusing into 2N $CoCl_2$ 6 H_2O in 10% gelatin Tube no 1 (left) silica; no 2, soft glass; no 3, hard Jena glass, no 4, tube lined with caoutchouc; no 5, lined with collodium, no 6, lined with coco butter, no 7, with paraffin, no 8, with lecithin (p 1521)
48 25N $AgNO_3$ diffusing into .25N NaCl in gelatin (p 1521)
49 5N $Pb(NO_3)_2$ diffusing into 1N K_2CrO_4 in agar Transverse section, detail of fig 51 and 52 (p 1522, 1528)
50 The same as fig 49, from a tube in which the periodicity was regular, as seen at the bottom of the figure (p 1522, 1528)

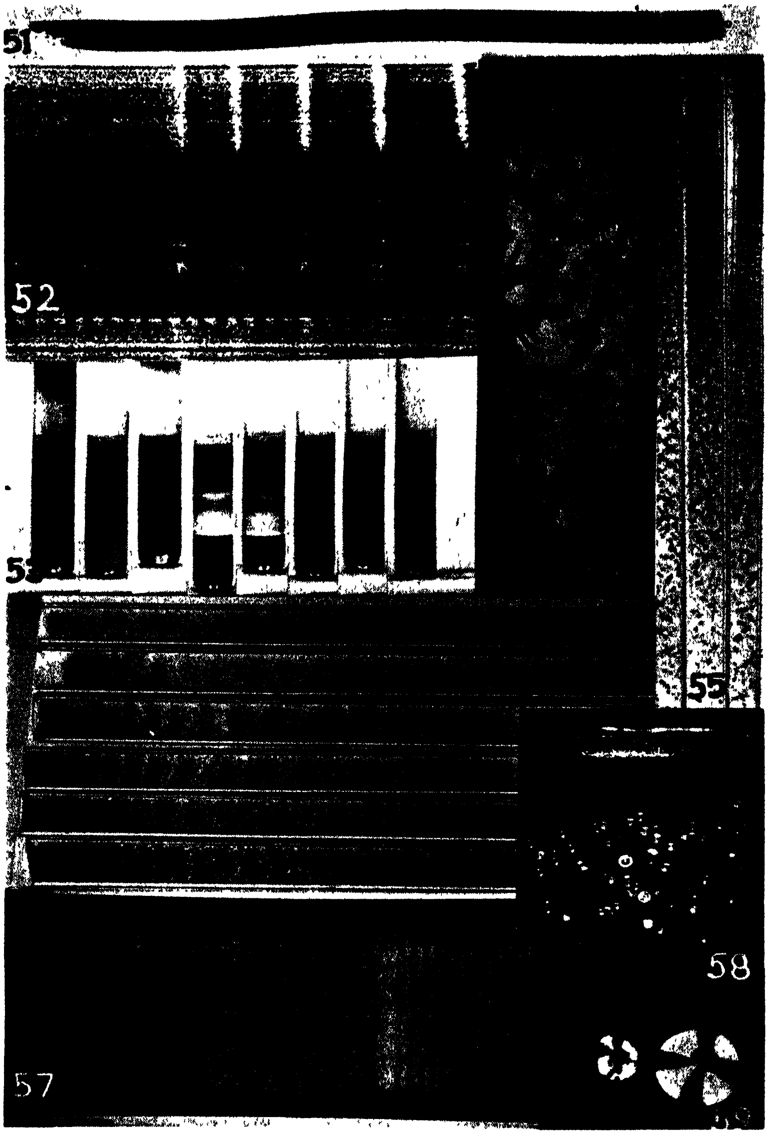


PLATE VII

51. .5N $Pb(NO_3)_2$ diffusing into .1N K_2CrO_4 in agar. (p. 1518, 1522, 1528)

52. The same as fig. 51. Detail—a portion of fig. 51 sectioned and more highly magnified (p. 1518, 1522, 1528)

53. NH_4OH diffusing into $CoCl_2$ in gelatin mixed with
   (a) distilled water (tube no 1 on the extreme left)
   (b) 1% sodium oleate
   (c) 0 1% sodium oleate (tube 3); saturated solution capryl alcohol (tube 4); 1 saturated solution capryl alcohol (tube 5); 0.3% cholesterol (tube 6), 0.03% cholesterol (tube 7); 0.003% cholesterol (tube 8). (p. 1523)

54. 2% ammonium oxalate diffusing into 2% $CaCl_2$ in gelatin. (p. 1523, 1530, 1542)

55. The same, at lower magnification. (p. 1523, 1530, 1542)

56. .5N K_2CrO_4 diffusing into .1N-.0062N $AgNO_3$ in starch. The highest concentration below. (p. 1527)

57. .5N $Pb(NO_3)_2$ diffusing into .0062N K_2CrO_4 in agar. Diffusion hindered by a bubble (the black mass at the left). (p. 1518, 1526, 1543)

58. 1N $Pb(NO_3)_2$ diffusing into 1N NaCl in gelatin. (p. 1524)

59. The same. Detail, between crossed Nicols. (p. 1524)

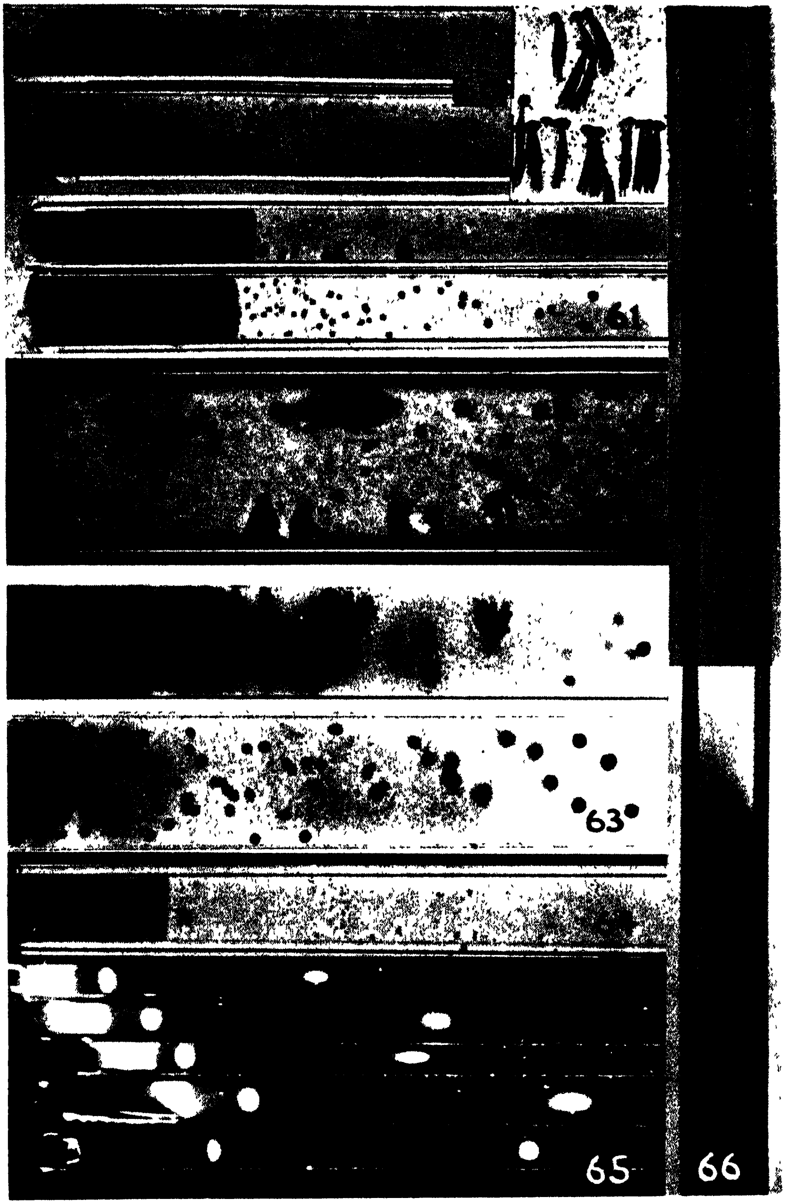


PLATE VIII

60 .5N $K_2Cr_2O_7$ diffusing into 0.1N $AgNO_3$ in starch 1.5 hours diffusion (p. 1524, 1540) Inset. 50% $AgNO_3$ diffusing into 2% $K_2Cr_2O_7$ in agar. See fig. 103a and b (p. 1524)

61 .5N $K_2Cr_2O_7$ diffusing into 0.1N $AgNO_3$ in starch, later. (p. 1524, 1540)

62. The same, detail. (p. 1524)

63 The same, later, when chemical alteration is overtaking the dark red precipitation membranes (p. 1524, 1540)

64 .5N $K_2Cr_2O_7$ diffusing into 0.125N $AgNO_3$ in starch, showing vague but evident periodicity (p. 1524, 1540)

65 NH_4OH diffusing into $MgCl_2$ in gelatin. Compare with fig. 3. (p. 1524)

66 4% $Pb(NO_3)_2$ diffusing into 4% KI in gelatin. (p. 1524)

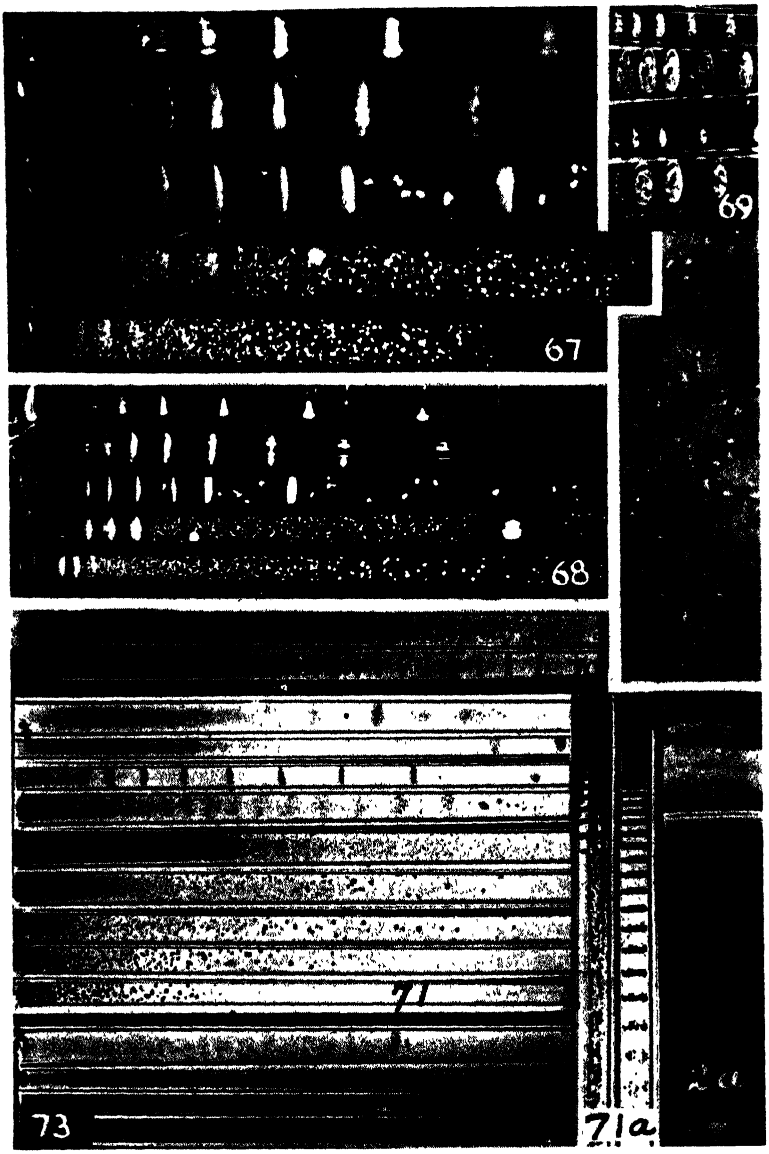


PLATE IX

67 $2N(NH_4)_2HPO_4$ diffusing into 1N-0062N $CaCl_2$ High concentrations below (p. 1524, 1529, 1541)

68. The same, later (p 1529, 1541)

69 The same, oblique view of zones. (p. 1529)

70 Lower tube: 1N $AgNO_3$ diffusing into 0031 $K_2Cr_2O_7$ + 0031 NaCl in gelatin. (p. 1526)
Upper tube: 1N $AgNO_3$ diffusing into 0031 NaCl in gelatin (p 1526)

71. .1N $AgNO_3$ diffusing into 1N-00035N (9 concentrations) Na_2HPO_4 in gelatin See fig 86. (p 1525-6, 1529)

71a $AgNO_3$ diffusing into $K_2Cr_2O_7$ in gelatin previously treated with $AgNO_3$ and $K_2Cr_2O_7$, the latter finally in sufficient excess (p 1525)

72 2% $CaCl_2$ diffusing into 2% ammonium oxalate in gelatin. (p 1523, 1542)

73 1N Na_2HPO_4 diffusing into 2N-025N $AgNO_3$ in gelatin (p 1525, 1530)

2a. See plate I.

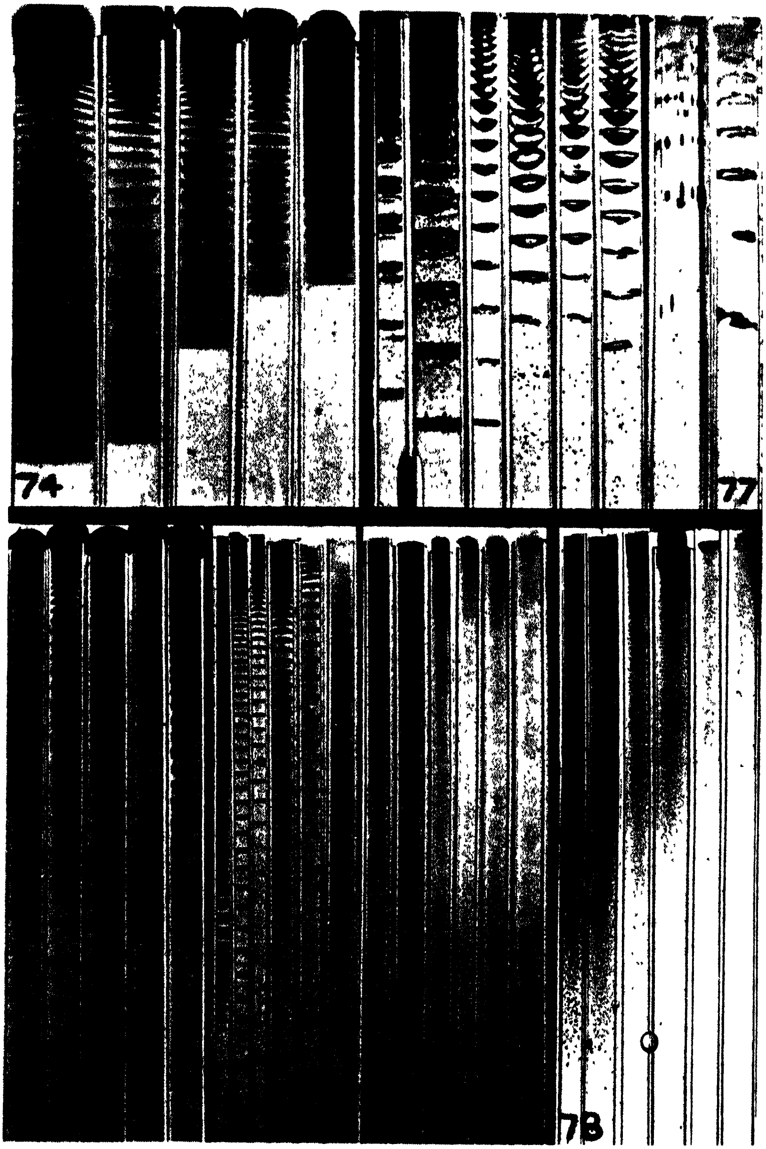


PLATE X

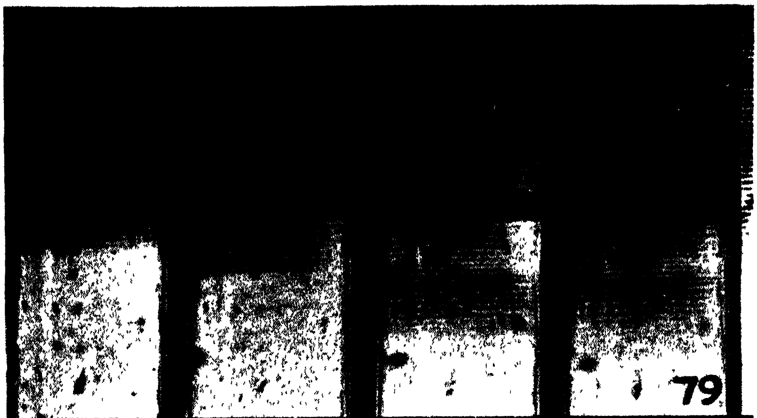
74 1 25N $AgNO_3$ diffusing into 0 1N- 0062N $K_2Cr_2O_7$ in gelatin Dark bands are red adsorbed on fine white bands Highest concentrations on the right (p 1526, 1528, 1530, 1541)

75 The same, later (p 1526, 1539)

76a. 5N $AgNO_3$ diffusing into 1N- 0031N K_2CrO_4 in gelatin
b 5N $AgNO_3$ diffusing into 1N- 0031N K_2CrO_4 in starch
The highest concentrations are on the left (p 1527, 1530, 1543)

77 5N K_2CrO_4 diffusing into 1N- 0125N $AgNO_3$ in gelatin High concentration on left (p 1520, 1526, 1543)

78 5N $AgNO_3$ diffusing into K_2CrO_4 in agar High concentration on the left (p 1527)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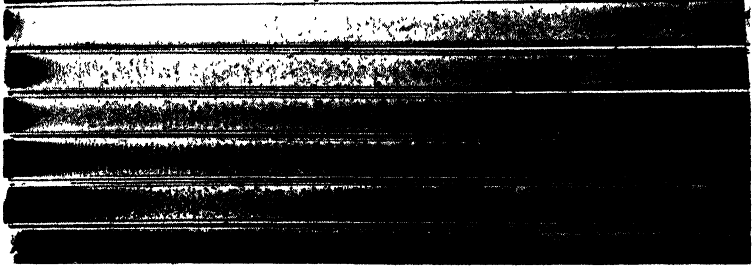


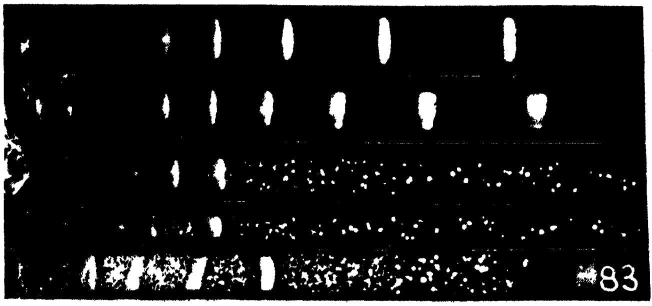
Plate XI

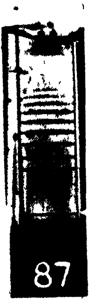
79. .5N $AgNO_3$ diffusing into 2% $K_2Cr_2O_7$ in gelatin. Four stages of the same tube (p 1528, 1539)

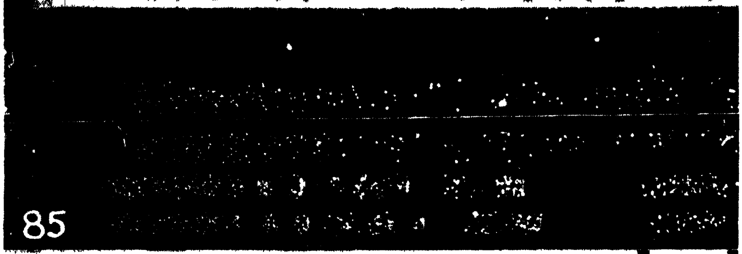
80. .25N $Pb(NO_3)_2$ diffusing into .1N-.006N $K_2Cr_2O_7$ in gelatin Upper two tubes .1N, second two tubes .05N; third, fourth and fifth .025N, .0125N and 0062N, respectively. (p. 1518, 1528)

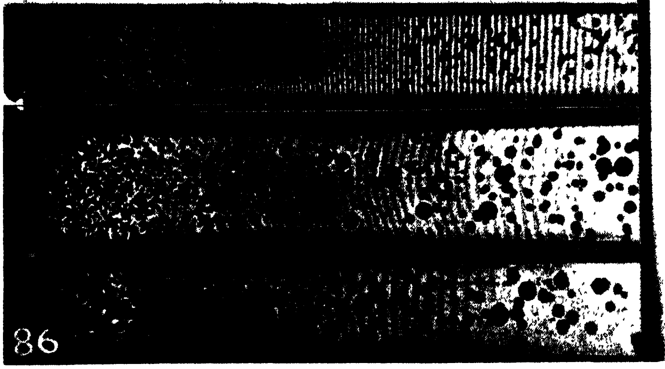
81. .2N Na_3PO_4 diffusing into 1N $CaCl_2$ in gelatin. (p 1529)

82. .5N $AgNO_3$ diffusing into .1N-.0031N $K_2Cr_2O_7$ in starch (p 1528)









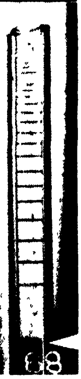


Plate XII

83. 2N Na_2HPO_4 diffusing into .05N-.0031N $CaCl_2$ in gelatin. High concentration below (p. 1529, 1541)

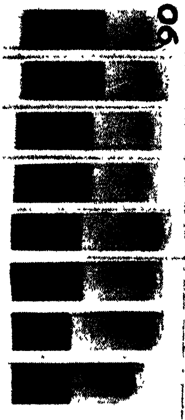
84. The same, later High concentration below (p. 1529, 1541)

85. .5N $NH_4H_2PO_4$ diffusing into 1N-.0031N $CaCl_2$ in gelatin High concentration below (p. 1529)

86. .1N $AgNO_3$ diffusing into 1N .025N Na_2HPO_4 in gelatin Three concentrations, the highest below See fig 71 (p. 1525, 1529)

87. .1 saturated solution NH_4OH diffusing into .5% $Co(NO_3)_2$ in gelatin. The dark line marked by the white triangle is the head of the diffusion column (p. 1537)

88. The same, later The head of diffusion column marked by white triangle (p. 1537)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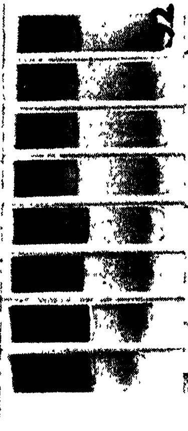
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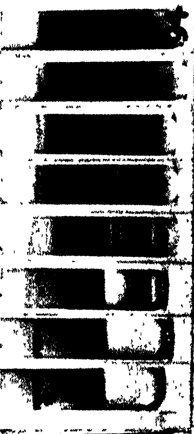
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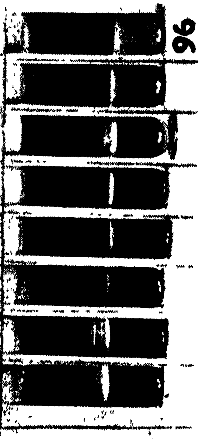
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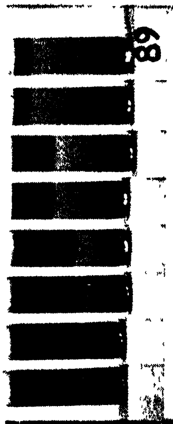
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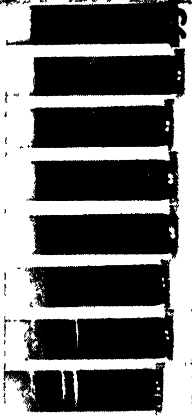
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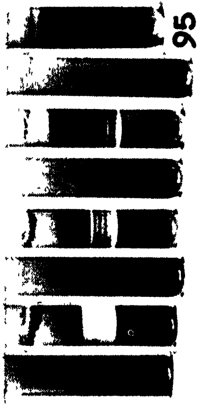
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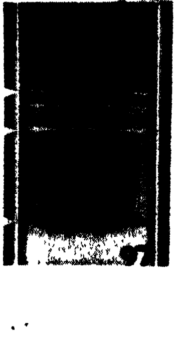
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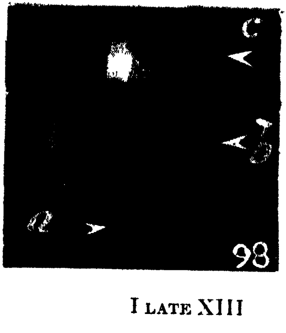
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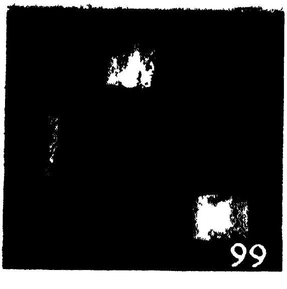
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PLATE XIII

PLATE XIII

89 25%, 20%, 10% and 5% NH_4OH diffusing into 2N $CoCl_2.6H_2O$ in 2.5% agar. Highest concentration to the left, 2 tubes for each concentration. (p. 1531)

90 10%, 15%, 20% and 25% NH_4OH diffusing into 2N $CoCl_2$ in 10% gelatin. Lowest concentration to the left, two tubes for each concentration. (p. 1531)

91 20% NH_4OH diffusing into 2N, 1.5N, 1N and 0.5N $CoCl_2$ in gelatin. Highest concentration to the left, two tubes for each concentration (p. 1531)

92 20% NH_4OH diffusing into 2N $CoCl_2$ in gelatin. Tubes 1 and 2 (to the left) kept at 24° C; 3 and 4 at 15-17° C; 5 and 6 at 7° C; 7 and 8 at 3° C (p. 1532)

93 20% NH_4OH diffusing into 2N $CoCl_2$ in 10% gelatin to which had been introduced 2N, 1.5N, 1N, 0.5N, 0.25N, 0.1N, 0.05N NH_4Cl and control to the eight tubes respectively, reading from left to right (p. 1533)

94 The same, after 10 days (p. 1533)

95 Tube no. 1, 4N NH_4Cl (extreme left hand tube)
2 " " plus 20% NH_4OH
3 2N "
4 " " " " "
5 1N "
6 " " " " "
7 .2N "
8 " " " " "

diffusing into 2N $CoCl_2$ in 10% gelatin (p. 1533)

96 20% NH_4OH diffusing into 2N $CoCl_2$ in 10% gelatin, to which was added the following chlorides in 1N concentration. Tube no. 1 (left hand), Li; no. 2, Na; no. 3, K; no. 4, Rb; no. 5, Cs; no. 6, Ca; no. 7, Sr; no. 8, Ba (p. 1534)

97 .25N $HgCl_2$ diffusing into .025N KI in gelatin in darkness, but exposed to light for 39 minutes at 16.25 o'clock (uppermost triangle), and for 37 minutes at 19.35 o'clock (lowermost triangle); middle triangle indicates 17.04 o'clock (p. 1532)

98 $HgCl$ and KI diffusing into each other, $HgCl_2$, from the left, KI from the right, in the following concentrations:

a. (top tube) saturated solution $HgCl_2$ and .25N KI

b. (middle tube) .5 saturated solution $HgCl_2$ and 1N KI

c. (bottom tube) .25 saturated solution $HgCl_2$ and .25N KI.

The points indicate the direction of the movement of the column of precipitate (p. 1534-6)

99 The same, later. (See diagram in the text.) (p. 1534-6)

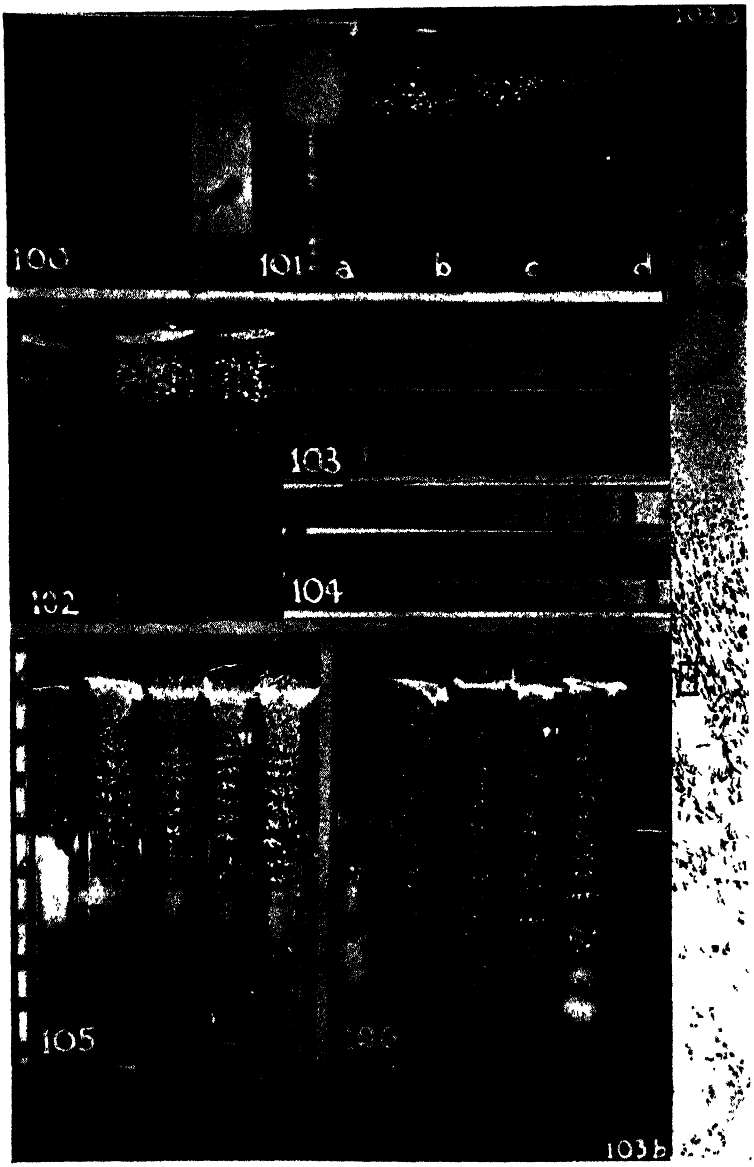


Plate XIV

100 .25N $AgNO_3$ diffusing into 05N Na_2CO_3 in gelatin. Head of diffusion column at arrow point. (p 1537)

101. 25N $Pb(NO_3)_2$ diffusing into 25N NaCl in gelatin In tube d, the single crystalloid arose 34 days from the beginning of the experiment and 29 days later than tube c Tubes a and b, earlier stages of a parallel series, . (p 1537)

102. The same, but another series (p 1537)

103. $AgNO_3$ diffusing into $K_2Cr_2O_7$ in gelatin (p. 1539)

103a. The same, but agar. Poured plate. (p 1527)

103b. The same, an earlier stage of diffusion, showing the colorless zone See fig 60, inset (p 1555)

104. 1.25 $AgNO_3$ diffusing into 0.1N- 025N $K_2Cr_2O_7$ in gelatin, photographed obliquely. (p. 1539)

105. .5N $Pb(NO_3)_2$ diffusing into 05N-.003N NaCl in gelatin High concentration on the left. (p. 1537)

106. The same, later.

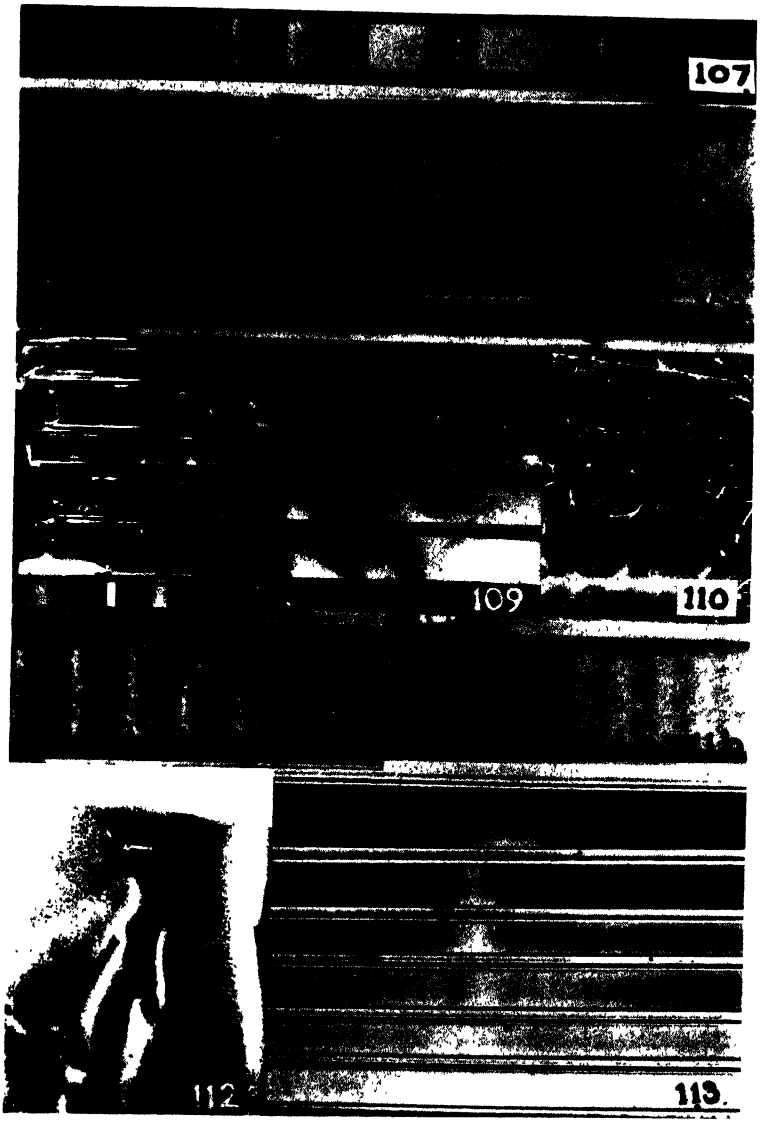


PLATE XV

107. 2% $K_2Cr_2O_7$ diffusing into .5 $AgNO_3$ in gelatin. Red salts disappearing and yellow taking their place. The *last dark band on the right* only is red, the rest yellow. (p. 1540)

108. The same system, adsorption of red salts on the glass wall. The last dark band on the right is red, the rest yellow. (p. 1540)

109. .5N $AgNO_3$ diffusing into 2% $K_2Cr_2O_7$ in 10% (bottom tube), 5%, 2.5%, 1.25% and .62% agar (p. 1540)

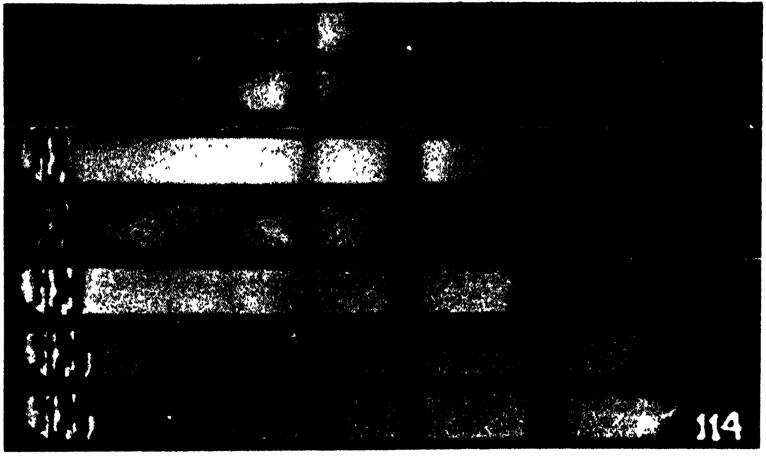
110. .5N $Pb(NO_3)_2$ diffusing into .5N NaCl in water in capillary space (p. 1513, 1541)

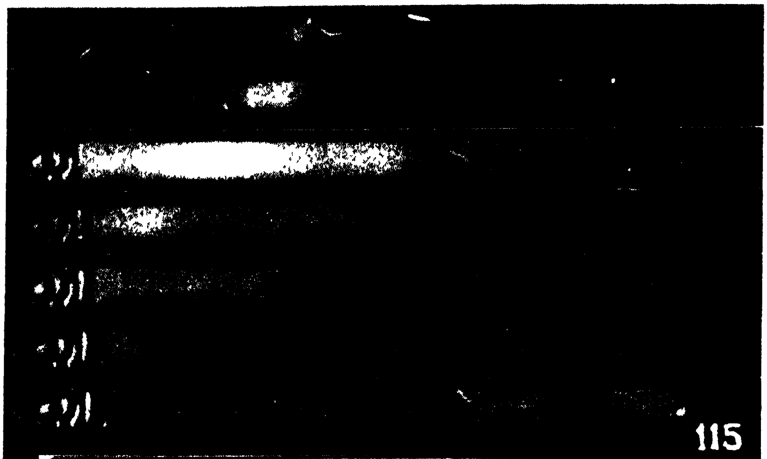
111a. 2% $Pb(NO_3)_2$ diffusing into $K_2Cr_2O_7$ in gelatin. (p. 1541)

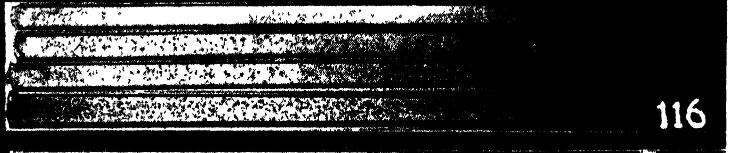
111b The same, earlier stage. (p. 1541)

112. 5N K_2CrO_4 diffusing into .05N $Pb(NO_3)_2$ in agar. (see figure 113). (p. 1518, 1528, 1542)

113. The same, the internal reagent in six concentrations: 112-.003N, the highest concentration above. (see figure 112). (p. 1518, 1528, 1542)







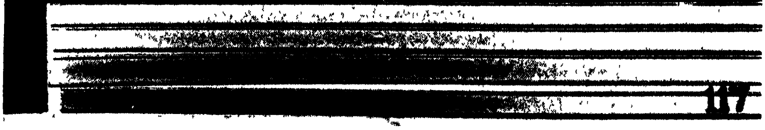


PLATE XVI

114 Selected "frames" from motion picture, viz exposures numbers 45, 66, 80, 103, 125, 154 and 166, reading from top 2% $Pb(NO_3)_2$ diffusing into 4% KI in 6% gelatin (p 1537, 1541, 1546)

115. Another tube of the same series. The sharp bands are white, the diffuse cloudy ppt yellow (p 1537, 1541, 1546)

116 .5N Ammonium oxalate diffusing into .1N-.025N $CaCl_2$ in gelatin (p 1543)

117. .5N $CaCl_2$ diffusing into 0.1N-.0125N Ammonium oxalate in gelatin (p 1543)

PHYSICO-CHEMICAL STUDIES ON PROTEINS

V. A Comparative Study of the Peptization of the Protein Complex in Various Seeds and Grains*

BY ERNEST V. STAKER AND ROSS AIKEN GORTNER

Historical

That certain proteins were soluble in saline solutions was first shown by Denis[1] in 1859. This observation was later confirmed by Hoppe-Seyler.[2] Denis observed that when sodium chloride extracts were made of both animal and vegetable tissue, certain proteinaceous substances were dissolved. While this discovery opened to chemists an entirely new means for isolating and purifying these proteins, its real significance was not appreciated until several years later.

In 1862 Ritthausen began his work on the vegetable proteins. For a number of years he devoted himself to the separation and purification of proteins and to their ultimate analysis. Ritthausen also became interested in that protein fraction which was extracted from seeds by weak alkaline solutions. As a result of these and other investigations, it became evident that the proteins in seeds existed in many diverse forms.

Weyl,[3] using the method of Denis, examined a large number of seeds and found that they all contained protein soluble in solutions of sodium chloride. Using his experiments as a basis, he divided the "globulin" thus extracted into two groups, the "vitellins," soluble in saturated solutions of sodium chloride, and the "myosins," insoluble in such solutions. Soon afterward, Vines[4] investigated the action of salt solutions on the aleurone grains in different seeds.

About this same time Weyl, who had been examining the data of others, made a severe criticism of Ritthausen's work. He maintained that the preparations which Ritthausen had obtained by extracting seeds with dilute alkali were altered products and that they did not represent the original constituents of the seed. Ritthausen soon afterward, however, showed that many of his preparations were largely or wholly soluble in saline solutions, and had for the most part retained unaltered their original solubility; also that the products obtained by direct extraction of seeds with neutral salt solutions agreed in many cases entirely with those he had previously described. Regardless of his assertion Ritthausen thought it best to apply the method of Denis to a number of seeds, especially those which he had previously studied, and he was able to show that most of the seed proteins were globulins The experience of others has since substantiated this conclusion.

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* Published with the approval of the Director, as Paper No. 998, Journal Series, Minnesota Agricultural Experiment Station. Condensed from a thesis presented by Ernest V. Staker to the Graduate School of the University of Minnesota, December, 1929, in partial fulfillment of the requirements for the degree of Dcotor of Philosophy.

It is difficult to understand why Ritthausen's preparations extracted from the seed by dilute alkali, and which he claimed to be of "highest purity" should later have been completely soluble in neutral saline solutions. If his samples had contained glutelins which are "insoluble" in salt solution but "soluble" in dilute alkali, they should not have become soluble in neutral salt solutions. One must conclude that either his proteins were almost wholly "globulins" and albumins and that no appreciable quantities of glutelins were present, or if originally present they had undergone partial hydrolytic cleavage into simpler fractions.

Thomas B. Osborne was the next investigator of importance in the field of the vegetable proteins. For more than twenty years he was primarily engaged in separating, classifying, and studying the protein constituents of seeds. His work included an extensive investigation not only of cereal grains but also of a large number of other kinds of seeds. Because of this fact the further historical review is divided into sections.

The Cereals

Barley.—As far as the authors are aware the salt- or water-soluble fractions of barley have been studied but little. Osborne[5] made the first preliminary survey. He observed that the seeds contained proteins which were soluble in water, in 10% sodium chloride, and in alcohol.

Osborne's conclusions from his investigation of the barley proteins were that "the barley contained 1 83% of nitrogen and if it be assumed that this all belonged to proteid matter with 17% of nitrogen, the flour would contain 10.75% proteids. The barley accordingly contained about 4.5% insoluble proteid, 4% of 'hordein' soluble in dilute alcohol, 0.3% albumin and 1.95% of globulin and proteose." If the albumin plus the globulin-proteose fraction is expressed in terms of the percentage of the total proteins, it is found that the total salt-soluble fraction amounts to 20.93% of the total protein. It will be noted also that the globulin fraction is 6.5 times that of the albumin fraction.

The only other paper since Osborne's studies on the salt-soluble proteins of barley, bearing directly on the subject, is that of Bishop[6] who recently reported some investigations on the composition and quantitative estimation of the barley proteins. His methods for the isolation of the globulin and albumin fractions are distinctly different from those employed by Osborne. Bishop extracted the seed meal with 5% potassium sulfate solution. The albumins in this extract were estimated by buffering the solution to pH 4.6 with an acetate-acetic acid buffer, and then coagulating the albumins at 82°C. The coagulum was filtered off and its nitrogen content determined. Total protein on the potassium sulfate extract was estimated by precipitation with trichloracetic acid and a subsequent nitrogen determination on the precipitate. The difference between the total protein nitrogen and the albumin nitrogen was assigned to "globulin" nitrogen.

Bishop found that approximately 34% of the total nitrogen in the seed was extracted when treated with 5% potassium sulfate solution. This is approximately 13% greater than was found by Osborne, although Osborne made his extractions with 10% sodium chloride, using very different experimental conditions. Sodium chloride usually, however, extracts a greater percentage of the total protein than does potassium sulfate when equal concentrations of the salts are used. The non-protein nitrogen reported by Bishop (11.5-16.3% of the total nitrogen of the seed) is unusually high for sound grain, so much so as to cast serious doubt on the validity of his albumin and globulin values. Bishop found the globulin fraction to be much less than the albumin fraction, although Osborne reported that there was 6.5 times as much globulin as albumin in barley. We believe that this discrepancy lies not in the difference in chemical composition of the samples used by these investigators, but in the different methods which they employed.

Oats.—Norton[7] as early as 1848 recognized three proteins in the oat kernel, 0.5-2.17% of an albumin, 15.76-17.72% of "casein" (or avenine), and 1.33-2.47% of gluten.

Von Bibra[8] claimed the protein constituents to be an albumin (1.24%) precipitated by boiling the cold water extract of ground oats, casein (0.15-0.17%) the product separating from the hot alcoholic extract on cooling, plant gelatin (3.00-3.25%) the substance soluble both in hot and cold alcohol, and nitrogenous substances insoluble in water and alcohol 11.38-14.85%.

Osborne[9] was the first to extract oats with water and with 10% sodium chloride solutions. He observed that such extracts had a strong acid reaction and that upon neutralization a precipitate formed which he called acid albumin After making several analyses of the water extract of oats he concluded that they contained (1) an acid albumin, (2) one or more globulins, and (3) a proteose which remained in solution after dialysis of the ammonium sulfate precipitate. The relative amounts of each of these stated either in terms of the weight of sample extracted or in percentage of the total nitrogen present, were not given.

In connection with his study of the oat kernel, Osborne's attention was called to the denaturizing effect of water. This was admirably demonstrated in the following experiment:

Osborne added 6 liters of water to 5 lbs. of "ground" oats. The mixture was allowed to stand over night when the supernatant liquid was decanted. Another 6 liters of water were added to the residual meal and the extraction repeated. The combined extracts were then saturated with ammonium sulfate, the precipitate separated from the remaining liquid, and suspended in water. This suspension was dialyzed in running water for 14 days. After filtering, the residue was extracted with a 10% sodium chloride solution, the solution again filtered and dialyzed. No precipitate of globulin formed, showing that all of the protein in the 10% sodium chloride solution was soluble in water. Osborne concluded that no globulin had been extracted from the substance which separated on dialysis of the aqueous extract, the globulin having been converted into an insoluble form. Osborne observed that such transformations were always the result of the use of water or salt solutions as contrasted with the use of alcohol, alkali, or heat: three agents known to suspend or destroy enzyme action. He therefore suggested that the reason for the apparent anomaly referred to above was that the water had permitted enzyme action to proceed.

From numerous and varied experiments on the oat proteins, Osborne finally concluded that the primary constituents were: (1) an alcohol-soluble protein amounting to 1.25% of the total protein of the oat kernel, (2) a globulin amounting to 1.5%, and (3) an alkali-soluble protein which made up the remainder with the exception of extremely small amounts of proteose and acid-albumin.

Wheat.—Most of the very early work on wheat has little bearing on the present problem and will therefore not be reviewed. We again turn to Osborne[10] for much of our knowledge regarding the proteins of wheat.

Osborne has made a rather detailed study of the globulin and albumin fractions from the embryo and endosperm portions of the kernel. By extracting 3000 grams of germ meal with 9 liters of water and heating the filtrate to 65°C., he obtained 279 grams of albumin or 9.3% of the oil-free germ meal. In another experiment germ meal was extracted with water, the solution adjusted to neutrality by the addition of alkali, and dilute calcium chloride solution was added as long as a precipitate formed. The clear filtrate when heated to 65° gave rise to a coagulum, which, when dried, amounted to approximately 3.4% of the oil-free germ meal. It will be noted that this figure is only about one-third of the value given in the former experiment. The difference in yields was probably due to varying experimental conditions.

An estimation of the globulin fraction in the above experiment gave a value of 9.17% or 2.67 times as much as the albumin. In another determination where the quantity of globulin in the embryo was estimated by extracting 200 grams of the meal with 2000 cc. of 3% sodium chloride, a value of 5.05% of globulin was obtained. Still other studies indicated that 9.5% of the embryo was leucosin (albumin), 4.84% globulin, and 3.03% proteose.

Like differences are to be noted in the albumin fraction extracted from wheat flour. In one experiment flour was extracted with 10% sodium chloride, the solution filtered and the filtrate saturated with ammonium sulfate. The supernatant liquid was filtered and heated at 60-65° for 1 hour. The resulting coagulum upon washing and drying formed 0.064% of the original meal. In another experiment exactly like the preceding, except that dialysis was employed to precipitate the globulin and the albumin in the filtrate was coagulated at 90° instead of 60°, Osborne obtained a yield of 0.16% albumin. Osborne further determined the globulin: albumin ratio in the meal obtained from the entire kernel of winter and spring wheats. The meals were extracted with 10% sodium chloride solution, the extracts dialyzed to separate the globulins and the albumin in the residual solution coagulated by heat. Spring wheat was found to contain 0.624% globulin and 0.391% albumin, giving a globulin: albumin ratio of 1.60. Similar figures for winter wheat were 0.625% globulin and 0.359% albumin with a ratio of 1.74.

Considering the differences which might have resulted from using two different classes of wheat, the results check very closely. But it must be emphasized that exactly the same method of procedure was used in each instance. This undoubtedly explains the very close agreement of the protein analyses of the two wheats.

Ladd[11] proposed a method for the determination of albumin and globulin in wheat and other cereals. Two hundred and fifty cc. of 1% sodium chloride solution was added to each 5 grams of flour. Total nitrogen was determined on a portion of the filtrate. To a like portion phosphotungstic acid was added, thus precipitating the true proteins and any organic nitrogen bases which may have been present in the extract. Nitrogen was then run on the filtrate, giving the "non-protein" nitrogen present in the extract. The albumin and globulin are then approximated by subtracting the non-protein nitrogen from the total nitrogen. This method assumes that only albumins and globulins are precipitated by phosphotungstic acid, whereas we know that other nitrogenous compounds including ammonia are precipitated.

Jones and Gersdorff[12] isolated and analyzed the globulin and albumin of bran. An extraction with water was first made at 1-2°C., using 20 cc. per gram of bran. This was continued until nothing more was removed. The combined extracts were dialyzed 12-14 days and the precipitated globulin removed. Further treatment of the filtrate with carbon dioxide eliminated the last traces of globulin. The filtrate was then boiled until coagulation of the albumin was complete. The residue from the water extraction was exhaustively extracted with 4% sodium chloride. The joint extracts were acidified with acetic acid and boiled until there was no further separation of globulin coagulum.

The percentage of the proteins isolated, expressed in terms of the total proteins in the bran, were: albumin, 16.64%; globulin, 13.62% with a globulin: albumin ratio of 0.83.

Bailey and Blish[13] made a study of the proteins extracted by diluted salt solutions from wheat flour. They estimate that only 48.3% of the protein nitrogen extracted by 1 per cent sodium chloride solution is referable to albumin and globulin, whereas 83.1% of the protein nitrogen extracted by 10% sodium chloride solution and 85.7% of the protein nitrogen extracted by 5% potassium sulfate solution are derived from albumin and globulin.

They believe that the extract of a patent flour when 1% sodium chloride is used as the solvent contains a large proportion of gliadin amounting to more than half of the total protein extracted. The extracts when 10% sodium chloride or 5% potassium sulfate solutions was used contained only 15% of the protein as gliadin. It was their conclusion therefore that 5% potassium sulfate solution should be used for the determination of the non-gluten proteins.

Hoffman and Gortner[14] have recently reported the results of some investigations in isolating the different proteins of wheat flour. The globulin fraction prepared by extracting flour with 5% potassium sulfate, and dialyzing the extract free of sulfate, was found to be practically insoluble in either 5% potassium sulfate or 10% sodium chloride solutions. It was soluble, however, in 0.2% sodium hydroxide. This product was designated as "globulin A." Since they thought that they might not have been dealing with a globulin in this experiment, another preparation was attempted using 10% sodium chloride solution. This was called "globulin B." This product was found to be nearly all soluble in 10% sodium chloride solution. They point out the possibility that the dialysis of the final preparation may have been carried too far, thus causing a protein→protean transformation.

The filtrates after the globulins had been removed, were concentrated in vacuo and the albumins isolated by exactly the same procedure. The filtrate from "globulin A" yielded 21 grams of albumin and that from "globulin B" approximately 1 gram. Thus 5% potassium sulfate extraction gave a globulin: albumin ratio of 0.28, whereas 10% sodium chloride extraction gave a ratio of 3.0. The difference in these ratios must lie in the methods followed, since the same flour was used in both cases. In discussing these differences the authors add: "Certain experiences in making the separations reported in this paper, together with subsequent experience to be reported later, make us strongly doubt whether or not any apreciable amount of a true globulin exists in patent wheat flour. We are certain that if a globulin is present it is in extremely small amounts. We are equally certain that no appreciable amount of proteose was present in the sample of flour which we examined."

Corn.—To Gorham[15] must be given the credit for our first reference to the proteins of corn. From evaporating a clear alcoholic extract of corn, he obtained a yellow wax-like substance to which he gave the name "zein." He described zein as resembling gluten but differing from it in not containing any nitrogen, the nitrogen content being overlooked in his methods of analysis. Other early contributions were the observations of Ritthausen[16] concerning "maize fibrin," a substance soluble in alcohol, and the bare statement made by Th. Weyl[8] that "powdered seeds of maize yield to a 10% solution of sodium chloride a globulin-like substance which, after purification by repeated precipitation with water and resolution in 10% sodium chloride, coagulates at 75°."

Nothing further was done until Osborne[17,18] took up the question. He used as usual 10% sodium chloride for securing the saline extract. Osborne concluded that the maize kernel in addition to other proteins, contained three globulins, which together form 24.67% of the total nitrogen in the meal. It was his observation also that "through the long-continued action of strong solutions of salt, as ammonium sulfate, the myosin-like globulin, and the globulin with a still lower content of nitrogen, are changed into insoluble modifications, soluble, however, in 0.5% sodium carbonate solution from which they are precipitated by neutralization apparently as albuminates." This is evidence again of the denaturing action of water and salt solutions. Osborne also reached the conclusion that no true albumin existed in the maize kernel. This was a rather striking conclusion since he had found an albumin to be present in all the seeds previously examined.

Legumes

Beans (*Phaseolus* sp.).—Ritthausen[19] made water extracts of the white bean (*Phaseolus vulgaris*) as early as 1883. In the following year he made extractions with 2% sodium chloride. These were cleared by subsidence and the residues, when dry, were reported as forming 13.2 and 11.45%, respectively, of the meal.

Osborne[20] extracted samples of kidney bean meal with 10% sodium chloride and concluded that it contained about 15% phaseolin, 2% phaselin, and 20.6% alkali-soluble protein. The first two were classified as globulins.

No further studies on beans were made until 1897 when Osborne[21] again turned his attention to the *Phaseolus* species. This time it was the small, red bean (*Phaseolus radiatus*) commonly grown in Japan. From 2 kg. of the ground seed treated with 8 liters of 10% sodium chloride solution he obtained 92.23 grams of globulin or 4.6% of the total weight of the meal. The percentage of nitrogen in the bean meal was not recorded.

Jones *et al*[22] investigated the proteins of the lima bean (*Phaseolus lunatus*). A 3% sodium chloride solution, at room temperature, extracted 72.32% of the total protein in the meal or 15.31% of the bean meal. They also noted that the soluble salts occurring naturally in the seeds were sufficient to dissolve 15.13% of protein when the meal was extracted with distilled water in the proportion of 2.5 cc. of water per gram of meal. This was practically as much as was extracted by the 3% sodium chloride solution. By fractional precipitation with ammonium sulfate they secured two globulins, α and β, which formed 2.74 and 1.58% of the total protein, respectively. An albumin, amounting to 1.75 per cent of the meal or 8.26% of the total protein, was obtained by coagulating by heat the residues of a distilled water extract of the meal after all of the globulins had been removed. This percentage of albumin is considerably higher than that obtained from the other beans which have been studied.

The proteins of the Mung bean (*Phaseolus aureus* Roxburgh) have been investigated by Johns and Waterman.[23] This bean they found to contain 21.74% protein of which about 87.5% was extracted by a 5% sodium chloride solution. Experiments with aqueous sodium chloride in different concentrations indicated a 5% solution as the most effective extractant; it dissolved 19.0% of protein from the finely ground seed. This extract yielded two globulins (designated α and β) by fractional precipitation with ammonium sulfate and subsequent purification. These fractions were equal to 0.35 and 5.75%, respectively, of the dry meal extracted. Only traces of an albumin were found in the meal.

Peas, Lentil, Horse Bean, Vetch.—In the early literature legumin was commonly referred to as a substance extracted from seeds by caustic alkalies, and more or less altered by the action of the solvent. After Ritthausen had repeated a number of his experiments, he concluded that his former preparations were a mixture of two proteins, one soluble in salt solutions after dissolving in dilute potassium hydroxide and precipitated with acid, and the other originally soluble in salt solution but rendered insoluble in that fluid by treatment with alkalies. This latter substance Ritthausen called "legumin."

Osborne and Campbell[24] pointed out that legumin forms the chief protein constituent of the pea, lentil, horse bean, and vetch. Vetch contained approximately 10% of this protein. These seeds also contain a globulin called vicilin which is associated with legumin but difficult to separate from it. Osborne and Campbell found that when seeds containing legumin were extracted with water, the following percentages of that protein in terms of weight of the seed were dissolved: pea 4%, vetch 2.5%, lentil 10%, and horse bean 16%. Legumelin, an albumin, was found in all legumes studied with the exception of *Phaseolus vulgaris*. The pea contained 2%, vetch 1.5%, and horse bean 1.25%.

In another experiment,[25] where a large quantity of peas was extracted with 10% sodium chloride solution, a ratio of 1 part albumin to 3.42 parts of globulin was obtained. Unfortunately in many of his papers Osborne does not report the yields of his proteins. He was primarily interested in the nature of the proteins and in their analysis in contrast to the exact amount of the protein in the original biological material.

In their studies on the legume proteins Osborne and Harris[25] were able to show, "that from the pea, *Pisum sativum*, horse bean, *Vicia faba*, lentil, *Ervum lens*, and vetch, *Vicia sativa*, preparations of the globulin can be obtained which agree strictly in properties and composition with one another but are distinctly different from those obtained from seeds of the genus *Phaseolus* and other kinds of legumes."

In connection with his studies on the pea Osborne[26] made some 10% sodium chloride extractions of finely ground vetch. A globulin equivalent to 5.2% of the original meal was isolated. In another experiment, where water was used as the extracting agent the globulin equaled only 1.04% of the original meal.

Peanuts.—Until recently Ritthausen[27] was the only individual who had published any experimental work on the proteins of the peanut (*Arachis hypogea*). In 1880 this author extracted oil-free peanut meal with solutions of sodium chloride, potassium, calcium, and barium hydroxides. From the 10% sodium chloride extract he obtained 27% of globulin by saturating the diluted extract with carbon dioxide, or simply by diluting the extract with a large volume of water. Apparently the same globulin was obtained by acidifying the alkaline extracts with acetic or sulfuric acids. Ritthausen found no evidence of the presence of more than one globulin in the peanut.

The peanut meal used by Ritthausen had been dried over sulfuric acid in a desiccator and contained 10.18% of nitrogen or 56% of protein, using 5.5 as the nitrogen factor.

Lechnikov[28] found the total nitrogen in the peanut to be 9.1% of which 8.74% occurred as "albuminous substance," including albumin, gluten, and globulin.

Johns and Jones[29] extracted air-dried oil-free peanut meal containing 42% of protein (N × 5.5) with a 10% sodium chloride solution and found that about 32% of protein, based on the weight of the meal used, was dissolved at room temperature. When the temperature was raised to 40-50°C., the yield was not increased. Only a very small quantity of albumin was obtained.

Miscellaneous Seeds

Flax-seed.—Osborne[30] found that the proteins of ground flax seed which had been freed from oil by extraction with benzine or ether were largely soluble both in water and solutions of sodium chloride. He reported that flax seed contains a globulin precipitated by dialysis; a protein resembling both globulin and albumin precipitable by long-continued heating at 100°C., as well as by sodium chloride in the presence of acid; a proteose and peptone fraction, and a protein not extracted by sodium chloride but soluble in dilute alkali. Osborne states that "all attempts to determine the amounts of these substances failed because of change, while in solution, into non-proteid bodies. It was further found that the relative amount of the various proteids was very variable; it is almost certain that the more soluble forms were largely, if not wholly, derived from the globulin in consequence of alteration during extraction and separation." In one instance water extracted from 100 grams of meal, protein material equal to 10.5% of the weight of the meal. Forty grams of material, using a saturated sodium chloride solution as solvent, gave a yield of 3.7 grams of protein equal to 9.25% of the weight of the original meal.

Sunflower.—Prior to the work of Osborne, the only published observations on the proteins of the sunflower seed were made by Ritthausen[27] and by Vines.[31] By extracting with very dilute alkali, Ritthausen obtained from the finely ground oil-free meal 44.71% of protein. By treating with sodium chloride solution, diluting the extract with 5 volumes of water and passing carbon dioxide through the solution, the yield was 25.3%. He observed that a considerable part of the protein of the sunflower seed was insoluble in salt solutions but soluble in dilute alkali.

Osborne[32] extracted the oil-free sunflower meal with 10% sodium chloride solution and precipitated the protein by dilution, dialysis, or by saturating the solution with sodium chloride. He obtained 7.4% of a globulin, "edestin," and concluded that this was the principal protein of the seed.

Other seeds.—The salt- and water-soluble fractions of a number of other seeds have been studied. Johns and Chernoff[33] reported that distilled water at room temperature extracted 2.5% of protein from buckwheat flour, while 5 or 10% sodium chloride solutions extracted 4.5%. A 5% solution of magnesium sulfate extracted 3.8% of protein.

Jones *et al*[34] state that distilled water, 2% sodium chloride solution, and a 10% sodium chloride solution, extracted 15.0, 18.5, and 18.0% of protein, respectively, from the jack bean (*Canavalia ensiformis*). Johns and Finks[35] found that a globulin, obtained by extracting cocoanut meal with 10% sodium chloride solution, comprised 10% of the weight of the meal. Davies[36] observed that 25% of the total protein of the rape seed (*Brassica napus*) is extractable using a 10% sodium chloride solution. Other studies of this nature include those of Johns and Gersdorff[37] who studied the proteins of the cohune nut (*Attalea cohune*), that of Cajori[38] on proteins of the pecan nut, Jones[39] on proteins of the cantaloupe seed, and that by Takahashi[40] on the proteins of adzuki bean.

Proteins and the Lyotropic Series

The existence of the Hofmeister or lyotropic series of ions has been noted by Jaeger,[41] Frumkin,[42] Freundlich,[43] and others, under conditions where lyophilic or organic colloids were absent. Loeb[44] argued against such a series, at least in so far as protein behavior was concerned. However, Bancroft questioned the line of reasoning used by Loeb, and McBain stated: "The effects of the Hofmeister or lyotrope (Freundlich) series of ions are too striking to be ignored. They have been observed with too many types of colloids in connection with too many systems not even containing colloids to be attributed to systematic experimental error."

Gortner, Hoffman, and Sinclair[45] were the first to emphasize the effect of salt solutions of various concentrations on the differential solubility or peptization of proteins. Twelve samples of wheat flour were studied, including flours milled from the most important commercial classes of wheats. At almost constant hydrogen ion concentrations (pH 5.0 to 6.0) a marked lyotropic effect was observed. It is evident that the hydrogen ion concentration *per se* could not have been playing the major role, and that such peptization differences as they observed must be attributed to some other factor.

Considering the percentage of total protein peptized by the potassium halides, they found a very definite lyotropic effect of the order $KF < KCl < KBr < KI$. Considering those salts which had potassium as the cation, they found for N/2 concentrations a series $F < SO_4 < Cl <$ tartrate $< CrO_4 < Br$; for N/1 concentrations $F < SO_4 < Cl <$ tartrate $< Br < I$; and for 2 N concentrations $F < Cl < Br$. The same relative order held for all the salts studied.

These authors further point out that the results as obtained were not due to hydrolysis since there was no increase in free $-NH_2$ and $-COOH$ groups. The phenomenon must therefore have been purely a colloidal one involving differential and more or less specific peptization behavior.

In conclusion they remark that "there is a lyotropic series of ionic effects in an aqueous system of protein and salts, and that these effects are due to properties of the anion and the cation of the salt and are observable and measurable even at a constant hydrogen-ion concentration."

Pascoe, Gortner, and Sherwood[46] made extracts of various flour streams, using 0.5N solutions of KBr, KCl, KF, and $MgSO_4$. The grades of flour ranged from first break to bran and shorts duster. The data as presented substantiated in all respects the findings of Gortner, Hoffman, and Sinclair. Without a single reversal the ionic effect was $F < Cl < Br$.

Although the flours used differed not only among themselves in chemical composition and physical properties, but from normal wheat flours as well, the same distinct lyotropic effect as encountered by Gortner *et al* was manifest throughout.

Very few pure proteins have been studied in relation to their solubility in solutions of different salts. Osborne and Harris[47] were the first to make such a study. They investigated the action of salts on the globulin edestin obtained from hemp-seed. This protein had been very carefully prepared in a pure crystalline state and was wholly insoluble in water.

Two grams of the air-dried preparation were suspended in a glass-stoppered bottle by adding a known quantity of a molar salt solution and sufficient water to make the final volume 20 cc. The mixture was then agitated at 20° for an unstated length of time and the undissolved globulin allowed to settle. Ten cc. of the clear solution was drawn out with a pipette, its nitrogen content determined, and from this the amount of dissolved edestin calculated. By using successively larger quantities of the molar salt solution and correspondingly less water, a series of determinations was made. The amount of edestin, in every case, was in decided excess of that dissolved, so that presumably as nearly complete saturation of the solution as was possible, under the conditions of the experiment, was attained.

The chlorides of the monovalent bases sodium, potassium, and caesium were found to have very nearly the same solvent power. The divalent bases, barium, strontium, calcium, and magnesium, dissolved approximately twice as much edestin as the monovalent chlorides. The solubility in general was observed to be independent of the nature of the base, but proportional to the number of chlorine atoms. Lithium chloride proved to be the only exception, its solvent power being much less than that of the other monovalent chlorides.

The effect of sulfates on the solubility of the globulin was very similar to that of the corresponding chlorides of the divalent bases. A half-molar solution of sodium sulfate dissolved edestin freely while a full-molar solution dissolved scarcely any. With potassium sulfate the same effect was noticed, but owing to its limited solubility precipitation of the protein did not take place. The curve for lithium sulfate followed those of potassium and sodium sulfate until the latter began to fall. With lithium sulfate, however, the amount of dissolved edestin remained practically constant with increasing concentration of the salt solution, and no evidence of diminishing solubility appeared. Magnesium sulfate, though commonly considered to precipitate globulins, when added in sufficient amount, followed the same course as that taken by the chlorides of the divalent bases.

Solutions of sodium and potassium iodide each had the same solvent effect, which was much greater than that of solutions of the bromides of the same molecular concentration, and slightly greater than that of the chlorides of the divalent bases. Sodium and potassium bromide had nearly the same solvent power, which was considerably higher than that of corresponding solutions of the chlorides. The bromides of barium and calcium also had practically the same solvent power. In this case, however, it was only a little greater than that of the bromides of the monovalent bases, and was distinctly less than that of the chlorides of the divalent bases or of the sulfates. Lithium bromide, like lithium chloride, had less solvent power than the corresponding solutions of sodium and potassium bromide, but the same solvent power as solutions of sodium chloride of the same molecular concentration.

Osborne and Harris point out the similarity between the solubility of edestin in solutions of salts of strong bases with strong acids and that of the solubility of certain insoluble inorganic salts in solutions of other salts due to the formation of complex salts in solution. They, therefore, thought it reasonable to assume that soluble addition products of the globulin and salt were also formed, a suggestion which had previously been made by Pauli.

In commenting further[48] on the problem of the solubility of proteins in salt solution, Osborne says: "Attention is called to these observations in the hope that someone may extend these investigations to other proteins with a view to developing better methods for extracting proteins from seeds than those now employed which depend almost entirely on the use of sodium chloride."

The above remarks were given little thought for a number of years. At least no well-planned experiments were undertaken in that direction. Just recently Sinclair,[49] realizing that much knowledge might be gained by following Osborne's suggestions, made a study of the solubility (peptizability) of pure gliadin in solutions of neutral salts.

Sinclair showed that normal solutions of various neutral salts peptized various amounts of gliadin. A normal KI solution peptized larger quantities of protein than did a normal solution of KBr, while the latter possessed a greater peptizing capacity than did a N KCl solution. When gliadin was treated successively with N KI solution, there remained some protein that was not capable of being peptized with N KI solution. However, if this non-peptizable protein was purified by repeated precipitations from alcohol in the same manner as the gliadin had been originally prepared the protein was then capable of being further peptized by N KI solution. The insoluble residue remaining after gliadin had been peptized the first time was repurified from salts by dialysis followed by solution in dilute alcohol and reprecipitation by absolute alcohol and ether. Following such repurification, it was indistinguishable from the original gliadin as judged by its repeptization by KI solution, analysis, etc.

Experimental

The Problem.—A review of the literature has disclosed the following points: (1) No systematic study has ever been made of the peptization of the proteins of seeds except those found in wheat flour and the protein, edestin (hemp seed); (2) There is a lack of quantitative data on the percentage of the total nitrogen extracted from seeds by water and by salt solutions; (3) The proportion of globulin to albumin in seeds has not been sufficiently studied; (4) Where such ratios have been computed using the data of other investigators, and considering the same kind of seed, a great variation has been noted. The investigation of the above problems, in so far as time would permit, formed the basis for the experiments reported in the following pages.

The Materials.—The seeds used were so chosen as to represent a number of the botanical families. In addition, they were selected so as to have them differ as widely as possible in their physical and chemical characteristics. They varied from 1.859 to 8.330 in percentage total nitrogen; from 1.850 to 70.72% in ether extract; and from 1.69 to 8.45% in ash content.

The plants from which the seed was obtained are listed below, grouped in accordance with the family represented.

Cereals	
Barley	*Hordeum vulgare*
Oats	*Avena sativa*
Triticum species	
Alaska	*Triticum turgidum*
Einkorn	*Triticum monococcum*
Emmer	*Triticum dicoccum*
Club	*Triticum compactum*
Durum	*Triticum durum*
Marquis and Quality	*Triticum vulgare*
Polish	*Triticum polonicum*
Spelt	*Triticum spelta*
Leguminosae	
Common alfalfa	*Medicago sativa*
Navy bean	*Phaseolus vulgaris*
Alsike clover	*Trifolium hybridum*
Andes Pea	*Pisum sativum*
Peanut	*Arachis hypogea*
Vetch	*Vicia angustifolia*
Cruciferae	
Mustard sp.	
Radish	*Raphanus sativus*
Rape	*Brassica napus*
Miscellaneous	
Yellow dent corn	*Zea mays*
White Ural millet	*Panicum miliaceum*
Sweet sorghum	*Andropogon saccharatus*
Teosinte	*Euchlaena Mexicana*
Brazil nuts	*Bertholletia excelsa*
Red Wing flax	*Linum usitatissimum*
Hemp	*Cannabis sativa*
Russian sunflower	*Helianthus annus*

Brazil nuts, radish, and vetch seeds were purchased on the open market. Those of hemp, teosinte, peanut, and vetch, were available at our own laboratories. The Alaska, White Polish, and Little Club varieties of the cereal grains were obtained through the courtesy of Dr. J. L. St. John, of the Washington State Agricultural Experiment Station. The remainder of the seeds or grains were furnished by the Department of Agronomy, University of Minnesota.

The seeds used had not been processed in any way and were in their natural state when secured. The seeds were bright in color and fully matured.

All samples before grinding were cleaned of dirt and other foreign material. As an extra precaution, and to make sure that the seed was all of one kind and type, the samples were "hand-picked."

In experiments involving the peptization of a plant material the necessity of standardizing the particle size is obvious. A survey of the literature showed that only one study had been made of the relation of particle size to the percentage of salt-soluble nitrogen. Bishop[6] observed that barley flour ground to pass a 1 mm. sieve yielded 25.6% of its nitrogen as "salt-soluble," when ground to pass a 1/2 mm. sieve this was increased to 31.2%, and when this material was reground in a "coffee mill" 36.2% of the nitrogen was extracted by the salt solution.

In our experiments it was thought best wherever possible to grind the samples sufficiently fine that they would all pass through a 100-mesh sieve. After grinding, the samples were thoroughly mixed so that uniform aliquots could be obtained. All samples were then stored at 0°C., until used.

A number of the seeds contained so much fat or oil as to make the fine grinding and sieving of the raw seed impracticable. Such seeds were first ground to a fineness commensurate with their oil content and then extracted in a large Soxhlet extractor with petroleum ether. After extraction and drying at room temperature, it was very easy to grind the material to the specified particle size.

The seed meals were analyzed for moisture, ash, and total protein. For the moisture determination 2-gram samples were dried at 100° to constant weight in the vacuum oven. Ash was determined on 5-gram samples, using the A.O.A.C. method. Total nitrogen was determined on 1-gram samples by the usual Kjeldahl-Gunning procedure.

The Methods.—(a) *Peptization of the Seed Proteins.*—The method used was essentially the same as that followed by Gortner *et al.*[45] Six grams of seed meal were weighed into a heavy-walled 100 cc. centrifuge tube and 50 cc. of the salt solution was added. The tube was then shaken in a mechanical shaker for exactly 30 minutes. Following the shaking, the meal was packed tightly in the bottom of the tube by whirling in a centrifuge, centrifuging being continued until the supernatant liquid was clear. This clear liquid was then carefully decanted into a Kjeldahl flask. After loosening the residue in the tube by means of a stirring rod, a fresh 50 cc. of salt solution was added, and a second extraction made in exactly the same manner as the first. The contents of the tube were again centrifuged and the clear supernatant liquid decanted into the same Kjeldahl flask. A third extraction was made in a similar manner. The nitrogen dissolved by the three successive salt extractions was then determined on the combined extracts by the usual Kjeldahl-Gunning method. Duplicate extractions were made in all instances. In case the usual limit of error for a Kjeldahl determination was exceeded, the extractions were repeated on fresh samples of meal until satisfactory analytical agreement was obtained. Half-gram samples were employed for the legumes and 1-gram samples for corn, in that section of the work where a comparison was made between the percentage of the total nitrogen peptized in unextracted meal and that in ether-extracted meal.

(b) *Extraction and Separation of the Albumin and Globulin Fractions.*—Ten-gram samples of the various meals were weighed into 250 cc. wide-mouth bottles and 200 cc. of distilled water was added. A single extraction of the meal was then made by shaking the bottle in the mechanical shaker for 2 hours and centrifuging as usual. Total nitrogen was then determined in duplicate on 25 cc. aliquots of the clear supernatant liquid. A 100 cc. portion of the supernatant liquid was placed in a cellophane dialyzing tube, and dialyzed against repeated changes of distilled water for 60 hours (room temperature) using toluene as a preservative. Upon completion of the dialysis, the contents and washing of the casing were poured into a beaker and the resulting mixture filtered. The filtrate and washings from the precipitate were caught in a 250 cc. volumetric flask, the solution made up to volume and total nitrogen determined in duplicate on aliquots.

Only in the case of flax was it necessary to use the centrifuge instead of a filter to separate the globulin from the albumin liquid. The water extract of the flax meal contained so much gummy material as to make filtering impossible.

The meal residue remaining from the original water extract was treated twice more with 200 cc. portions of distilled water. As usual the bottles were shaken two hours for each extraction and then centrifuged. These extracts were discarded. It was assumed that such a procedure would remove the remainder of the albumin contained in the sample and that whatever protein might be dissolved by further treatment with salt solutions would be globulins. Accordingly, the meal residues remaining after three water extractions were subsequently treated with M/2 KCl solution. In order to make the results strictly comparable to those where salt extractions had been made on 6-gram samples, 85 cc. of the salt solution was added to each sample. Three separate extractions of 30 minutes each were made and the extracts decanted into the same Kjeldahl flask and a total nitrogen determination was made.

The residues from the KCl extraction were re-extracted using 0.5 M KBr solution. Here again three extractions were made, the residues being treated each time with 85 cc. of the salt solution. These data form a part of that recorded in Table VI.

We have already noted in the historical review that different globulin: albumin ratios are frequently obtained where two different methods are employed

TABLE I

The Percentage of Total Nitrogen peptized from Seed Meals by Various M/2 Salt Solutions
Six-gram Samples used

Classification	Seed used	Moisture	Ash	Total Nitrogen	Total Nitrogen Peptized by***				
					KF	K_2SO_4	KCl	KBr	KI
		%	%	%	%	%	%	%	%
Cereals	Barley	7.80	3.13	2.634	24.50	27.77	28.51	31.84	33.33
	Oats	6.58	4.25	1.859	25.35	30.42	34.78	46.49	55.30
	Tr. Species (Av.)	9.67	2.09	2.76	24.86	26.24	30.98	40.16	55.01
	T. Vulgare (Av.)	10.04	1.90	2.288	29.79	31.61	36.88	46.14	57.02
Legumes	Common alfalfa*	8.08	3.81	6.044	49.68	65.05	59.08	66.74	73.69
	Navy beans*	12.66	3.96	3.768	82.41	83.26	85.45	84.29	90.61
	Alsike clover*	8.03	3.94	6.037	53.83	64.13	56.34	63.72	76.22
	Andes field pea*	10.46	3.51	4.215	85.23	83.93	84.05	88.33	95.18
	Peanut	8.89	4.37	8.242	65.99	89.19	86.09	89.51	93.19
	Vetch	8.72	2.84	5.266	70.66	73.08	71.49	74.48	77.96
Cruciferae	Mustard Sp.**	6.98	4.75	4.889	57.56	59.41	60.05	59.66	58.19
	Radish	7.31	4.31	5.774	72.36	73.11	74.74	76.57	77.43
	Rape	8.19	4.47	4.322	67.71	70.78	72.73	74.59	74.61
Miscellaneous	Yellow dent corn	8.48	1.81	1.98	19.39	19.72	19.72	21.38	22.01
	White ural millet	8.35	4.02	2.187	9.79	11.87	11.91	12.55	12.54
	Sweet sorghum	9.18	2.29	1.978	8.24	7.91	7.93	7.96	8.03
	Teosinte	6.01	2.69	1.880	6.22	6.42	6.39	7.05	7.69
	Brazil nut	8.81	5.96	5.323	81.58	82.46	82.13	82.97	83.19
	Red Wing flax	8.23	4.86	5.050	53.53	65.26	57.64	63.51	60.94
	Hemp	8.02	8.37	5.716	24.65	46.39	30.32	57.42	70.58
	Russian sunflower	7.07	3.24	2.849	41.18	49.44	56.00	58.67	64.90

* 0.5 grams samples.

** The values recorded for mustard are probably not representative of any single species, since the seed was undoubtedly a mixture of various mustard species.

*** The peanut, mustard, radish, rape, corn, flax, sunflower, and Brazil nut meals were extracted with petroleum ether prior to peptization of the meal by salt solutions.

TABLE II

Comparison of the Percentages of the Total Nitrogen in Extracts of Various Seed Meals

.Ten-Gram Samples Used*

Classification	Seed used	Nitrogen Water Extract A	Nitrogen remaining in Solution following Dialysis of Water Extract B	Nitrogen peptized by M/2 KCl following Water Extractions C	Globulin extracted by Water A−B=D	Total Globulin C+D=E	Total Albumin + Globulin B+E=F	Peptized by KCl (no water extraction) G	Globulin denatured G−F=H	$\frac{\text{Globulin}}{\text{Albumin}}$ D/B=I
		%	%	%	%	%	%	%	%	
Cereals	Barley	15.12	3.74	7.05	11.38	18.43	22.17	28.51	6.33	3.04
	Oats	16.77	1.73	6.62	15.04	21.66	23.39	34.78	11.38	8.69
				9.12**		24.16**	25.89**	46.48**	20.59**	
	Tr. species (Av.)	20.01	4.41	9.40	15.60	25.00	29.41	30.98	1.57	3.53
Leguminosae	Alfalfa	41.80	3.29	8.52	38.51	47.03	50.32	59.08***	8.76	11.70
	Navy beans	73.15	14.11	9.29	59.04	68.33	82.44	85.45	3.01	4.18
	Alsike clover	25.16	3.42	14.05	21.74	35.79	39.21	56.34***	17.13	6.36
	Andes field pea	78.87	10.86	10.09	68.01	78.10	88.96	84.05	−4.91	6.26
	Wild vetch	25.48	4.02	35.62	21.46	57.08	61.10	71.49	10.38	5.34
	Peanut	66.69	5.36	4.57	61.33	65.90	71.26	86.09	14.83	11.44
Cruciferae	Radish	49.67	8.46	21.58	41.21	62.79	71.25	74.74	3.49	4.87
	Rape	47.80	12.37	19.55	35.43	54.98	67.35	72.73	5.38	2.86
Mis-cellaneous	Yellow dent corn	12.59	3.34	7.17	9.25	16.42	19.76	19.72	−0.04	2.77
	White Ural millet	5.94	1.43	3.70	4.51	8.21	9.64	11.91	2.27	3.15
	Sorghum	8.29	0.83	0.42	7.46	7.88	8.71	7.93	−0.78	8.99
	Teosinte	4.98	0.83	0.92	4.15	5.07	5.90	6.39	0.49	5.00
	Brazil nut	35.33	8.40	37.94	26.93	64.87	73.27	82.13	8.86	3.21
	Red Wing flax	64.07	15.64	10.38	48.43	58.81	74.45	57.64	−16.81	3.10
	Hemp	13.63	1.31	9.51	12.32	21.83	23.14	30.32	7.18	9.40
	Russian sunflower	37.65	12.74	10.21	24.91	35.12	47.86	56.00	8.14	1.95

* The technic of extraction employed in this table differs from that employed in the case of Table I, in that in the present table a 10-gram sample was given a single extraction with 200 cc. of water (or salt solution) during a two-hour period.

** KBr extraction.

*** 0.5 gram samples used.

TABLE III

The Percentage of the Total Nitrogen Peptized from Various Wheat Meals by Distilled Water and by M/2 Salt Solutions

Wheat Variety	Moisture	Ash	Total Nitrogen	Total Nitrogen Peptized by					
				H_2O	KF	K_2SO_4	KCl	KBr	KI
	%	%	%	%	%	%	%	%	%
Alaska	9.73	1.96	2.729	19.58	21.86	23.74	28.29	38.07	54.80
Einkorn	9.37	2.22	2.891	17.89	22.39	23.27	27.67	36.28	56.42
Emmer	9.32	2.25	2.477	21.28	21.08	22.65	28.33	38.73	52.99
Little Club	10.57	2.25	2.99	19.72	25.97	27.10	30.61	38.76	53.55
Marquis	10.50	1.69	2.464	23.16	26.84	28.63	33.24	42.57	54.40
Mindum	10.47	2.25	3.017	21.58	24.93	26.01	30.91	41.18	58.09
Polish	8.34	1.81	3.64	18.34	21.97	23.20	27.39	36.42	55.53
Quality	9.58	2.11	2.112	26.72	32.74	34.59	40.53	49.72	59.65
Spelt	9.18	2.28	2.509	23.26	25.94	26.93	31.83	39.75	49.63
Average	9.67	2.09	2.76	21.28	24.86	26.24	30.98	40.16	55.01

in isolating the albumin and globulin fractions of a seed. To ascertain whether or not the same ratio of globulin to albumin would be found using a salt solution as was found in the distilled water experiments, the extractions were repeated on 10 grams of the seed meal of corn, millet, sorghum, and teosinte, extracting with 200 cc. of 0.5 M KCl solution. The method followed in the separation of the albumin and globulin fractions was exactly the same as that described above. Dialysis was continued until there was no further test for chloride in the dialysate. The data are shown in Table VII.

All data contained in the tables were computed on the moisture-free basis. Wherever extractions were made, the nitrogen thus dissolved was expressed in terms of percentage of the total nitrogen of the meal. In case the oil or fat had been removed previous to peptization this percentage was again added to the total dry matter and the results computed on that basis.

The Data.—The data are contained in Tables I to XI and in Figs. 1 and 2. The graphs, as diagrammed, are not mathematically correct, since there is only one variant. However, it is felt that for the purpose intended, they represent the data much better than would a graph of the "block" type.

TABLE IV

Relative Differences in the Percentage of the Total Nitrogen of Wheat Sorts which is peptized by Various Salts*

Wheat Variety	Difference between the Percentage of the Total Nitrogen Peptized by				
	K_2SO_4 and KF	KCl and K_2SO_4	KBr and KCl	KI and KBr	KI and KF
Alaska	1.88	4.55	9.78	16.73	32.94
Einkorn	0.88	4.40	8.61	20.14	34.03
Emmer	1.57	5.68	10.40	14.26	31.91
Little Club	1.13	3.51	8.15	14.79	27.58
Marquis	1.79	4.61	9.33	11.83	27.56
Mindum	1.08	4.90	10.27	16.91	33.16
Polish	1.23	4.19	9.03	19.11	33.56
Quality	1.85	5.94	9.19	9.93	26.91
Spelt	0.99	4.90	7.92	9.88	23.69
Average	1.38	4.74	9.18	14.85	30.15

* The first salt named in the column peptized the largest amount of nitrogen.

TABLE V

A Comparison of the Various Nitrogen Fractions expressed as per cent of the Total Nitrogen and the Albumin:Globulin Ratio obtained from the Extracts of Wheat Meals

Wheat Variety	Total Nitrogen peptized by: Water* (Albumins + Some Globulin in Soln.)	Water Following Dialysis (Albumins in Soln.)	M/2 KCl Following Water Extractions (Globulin)	Globulins extracted by Water	Total Globulin	Total Albumin + Globulin	Extraction originally by M/2 KCl (No water Extraction)	Globulin denatured by dialysis and which then appears in the Glutelin	$\frac{\text{Globulin}}{\text{Albumin}}$
	A	B	C	A−B=D	C+D=E	B+E=F	G	H	D/B
	%	%	%	%	%	%	%	%	
Alaska	19.18	4.70	8.71	14.48	23.19	27.89	28.29	0.40	3.08
Einkorn	16.67	2.77	10.91	13.90	24.81	27.58	27.67	0.09	5.02
Emmer	20.39	5.00	8.29	15.39	23.68	28.68	28.33	−0.35	3.08
Little Club	18.94	4.01	10.05	14.93	24.98	28.99	30.61	1.62	3.72
Marquis	21.21	7.04	8.08	14.17	22.25	29.29	33.24	3.95	2.01
Mindum	19.34	5.94	8.57	13.40	21.97	27.91	30.91	3.00	2.26
Polish	17.47	3.74	8.54	13.73	22.27	26.01	27.39	1.38	3.67
Quality	24.94	3.78	13.01	21.16	34.17	37.95	40.53	2.58	5.60
Spelt	21.92	2.69	8.42	19.23	27.65	30.34	31.83	1.49	7.15
Average	20.01	4.41	9.40	15.60	25.00	29.41	30.98	1.57	3.53

*The values in this column differ somewhat from values in the similar column of Table III, because a different technic was employed. In Table III the data represent the extractions of six-gram samples with three successive treatments of 50 cc. of water, each treatment with water being for 30 minutes. In the present table a *single* extraction with 200 cc. of water during a two-hour period was employed.

TABLE VI

The Percentage of the Total Nitrogen peptized from the Same Charge of Seed Meal using Successive Extractions with Different Reagents

Seed used	Total Nitrogen peptized by				Ratios		
	Distilled Water*	M/2 KCl following Water Extract†	M/2 KBr following Extraction by M/2 KCl‡	Total extracted	A/B	B/C	A/C
	A	B	C	A + B + C			
	%	%	%	%			
Barley	15.12	7.05	3.38	25.55	2.14	2.09	4.47
Alsike clover	25.16	14.05	2.79	42.00	1.79	5.04	9.02
Red Wing flax	64.07	10.38	4.50	78.95	6.17	2.31	14.24
Hemp	13.63	9.51	3.86	27.00	1.43	2.46	3.53
Oats (sample 1)	16.77	6.62	5.25	28.64	2.53	1.26	3.19
Oats (sample 2)	16.81	9.12**	2.58***	28.51	1.84	3.53	6.52
Wild vetch	25.48	35.62	6.88	67.98	0.71	5.18	3.70

* Ten-gram samples submitted to single extractions, using 200 cc. of water for a two-hour extraction period.

** KBr

*** KCl

† Residue from water extraction peptized with three successive portions of 85 cc. 0.5 M KCl, each treatment being for a period of 30 minutes.

‡ Residue from KCl extraction peptized with three successive portions of 85 cc. 0.5 M KBr, each treatment being for a period of 30 minutes.

TABLE VII

Comparison between the Globulin/Albumin Ratios when Extractions were made with 0.5 M KCl and Distilled Water, respectively

Seed Used	Fraction of Total Nitrogen peptized by M/2 KCl* A %	Nitrogen Remaining in Solution Following Dialysis of KCl Extract B %	Globulins A-B %	Ratios	
				Globulin / Albumin from KCl Extracts	Globulin / Albumin from Water Extracts (Table II)
Yellow dent corn	20.10	4.17	15.93	3.82	2.77
White Ural millet	11.57	1.96	9.61	4.90	3.15
Sweet sorghum	7.79	1.24	6.55	5.28	8.99
Teosinte	7.13	2.08	5.05	2.43	5.00

* The values in Column A differ from those in Table I and Column G, Table II, because of a somewhat different technic employed in the extraction. In Tables I and II, the data represent the extractions of six-gram samples with three successive treatments of 50 cc. of M/2 KCl, each treatment with M/2 KCl being for 30 minutes. In the present table a single extraction of 10 grams of the meal with 200 cc. of M/2 KCl during a two-hour period was employed.

TABLE VIII

Comparison of the Ratio of the Total Nitrogen peptized by M/2 KCl and M/2 KI, respectively, and the Percentage of the Total Protein appearing in the Globulin Fraction

Classification	Seed used	Ratio of KCl/KI	Total Globulin %
Cereals	Barley	0.855	18.43
	Oats	0.628	21.66
	Wheat (av.)	0.563	25.00
Leguminosae	Alfalfa	0.801	47.03
	Navy beans	0.943	68.33
	Alsike clover	0.739	35.79
	Andes pea	0.883	78.10
	Hairy vetch	0.917	57.08
	Peanut	0.923	65.90
Cruciferae	Radish	0.965	62.79
	Rape	0.974	54.98
Miscellaneous	Corn	0.895	16.42
	Millet	0.949	8.21
	Sorghum	0.987	7.88
	Teosinte	0.830	5.07
	Brazil nut	0.987	64.87
	Flax	0.945	58.81
	Hemp	0.429	21.83
	Sunflower	0.862	35.12

TABLE X

The Percentages of the Total Nitrogen peptized by M/2 Salt Solutions from Whole Seed Meals and from Seed Meals which had been exhaustively extracted with Ether

Seed Meal Used	Nature of Sample	Ether Extract removed	Percentage of Total Nitrogen peptized by:				
			KF	K_2SO_4	KCl	KBr	KI
		%	%	%	%	%	%
Navy beans	Whole meal	—	82.41	83.26	85.45	84.29	90.61
Navy beans	Extracted meal	1.85	86.71	88.97	87.94	88.48	93.10
Navy beans	Difference*	—	+4.30	+5.71	+2.49	+3.79	+2.49
Alsike clover	Whole meal	—	53.82	64.12	56.34	63.72	76.22
Alsike clover	Extracted meal	9.48	55.09	70.04	63.89	70.83	76.61
Alsike clover	Difference	—	+1.27	+5.92	+7.55	+7.11	+0.39
Andes field pea	Whole meal	—	85.22	83.94	84.05	88.34	95.18
Andes field pea	Extracted meal	1.45	85.59	91.22	89.33	90.15	95.13
Andes field pea	Difference	—	+0.37	+7.28	+5.28	+1.81	−0.05
Yellow dent corn	Whole meal**	—	15.84	16.69	16.92	18.48	19.96
Yellow dent corn	Extracted meal	4.30	19.16	19.29	19.24	20.13	21.47
Yellow dent corn	Difference	—	+3.32	+3.40	+2.32	+1.65	+1.51
Alfalfa	Whole meal	—	49.68	65.05	59.08	66.74	73.69
Alfalfa	Extracted meal	11.72	49.95	65.48	56.57	61.37	69.34
Alfalfa	Difference	—	+0.27	+0.43	−2.51	−4.37	−4.35
Hemp	Whole Meal	—	24.65	46.39	30.32	57.42	70.58
Hemp	Extracted meal***	0.61	26.17	64.44	41.54	63.69	71.55
Hemp	Difference	—	+1.52	+18.05	+11.22	+6.27	+0.97

* A + sign indicates that a greater peptization of the proteins occurs in the ether-extracted meal.

** These values for corn differ from those reported in Table I probably because of the fact that the meal used in the extractions reported in Table I had been extracted with petroleum ether.

*** The "whole meal" was from a larger lot originally prepared in our laboratories for other purposes. It had been washed in gasoline to remove the greater proportion of the oil so as to prevent rancidity.

TABLE IX

Comparison of the Ratio of the Total Nitrogen peptized by M/2 KCl and M/2 KI, respectively, and the Percentage of the Total Protein appearing in the "Globulin" Fraction

Wheat	Ratio of KCl/KI	Total Globulin %
Alaska	0.516	23.19
Einkorn	0.490	24.81
Emmer	0.534	23.68
Little Club	0.571	24.98
Marquis	0.611	22.25
Mindum	0.532	21.97
Polish	0.493	22.27
Quality	0.679	34.17
Spelt	0.641	27.65

Discussion

Peptization of the Proteins of Barley and Oats.—The first part of Table I shows the percentage of the total nitrogen peptized for the grains, barley and oats. The same data are illustrated graphically in Fig. 2. A very definite lyotropic effect of the order $KF < K_2SO_4 < KCl < KBr < KI$ is noted, the same order being followed by both grains. In every case, however, a greater percentage of the total nitrogen of oats is peptized than is the case with barley. It will be further noted that a M/2 solution of KF peptizes almost the same percentage of the total nitrogen of both cereals. However, as we proceed from the salt which peptizes the smallest amount (KF) to that peptizing the largest (KI), the difference between the same salts becomes increasingly greater. Thus the difference between the fluorides is 0.85%; between the sulfates 2.65%; the chlorides 6.27%; the bromides 14.65%; and the iodides 21.97%. The peptization range of barley is from 24.50% (KF) to 33.33% (KI), a difference of only 8.83%. When the same comparison is made with oats it is found to be from 25.35% (KF) to 55.30% (KI), a difference of almost 30%.

A glance at the graph illustrating these relationships shows that almost a straight line can be drawn for oats when the halogen salts are considered. Such a line cannot be drawn for barley, as all the points are best connected with a curved line. It will also be observed that the behavior of the proteins of oats toward salt solutions resembles that of the proteins of wheat. In fact if the curve for oats is compared with that for the average of the *Tr. vulgare* group of wheats, a very similar relationship is seen.

The question at once arises as to why the proteins of these cereals react so differently. It is evident that since the proteins from these grains were subjected to exactly the same kind of treatment, the differences found must be attributed largely to the properties of the proteins themselves. Other factors could enter which might influence the total amounts peptized by the various salts, but it is difficult to see how these would account for the difference in behavior when one cereal is compared with another. Reference is made here especially to the fat content of the seeds, a point which will be considered later.

If the chromosome numbers of barley, oats, and wheat are compared in relation to the peptization curves for these cereals, another relationship may be seen. The cultivated varieties of barley have 7 chromosome pairs, those of oats 21 and the *vulgare* species of wheats 21. The curve (Fig. 2) showing the average peptization for all the types or varieties of wheats is observed to be about midway between that for the *vulgare* class and the curve for barley. The only exception to this is the upper part of the wheat-average curve. Reference to Fig. 1 will show that it is those wheats which have the lower number of chromosomes, either 7 or 14, that bend the wheat-average curve toward the curve for barley. One might conclude then, that as far as the data presented here are concerned, ease of peptization of the wheat proteins seems to be associated with a correspondingly larger number of chromosomes.

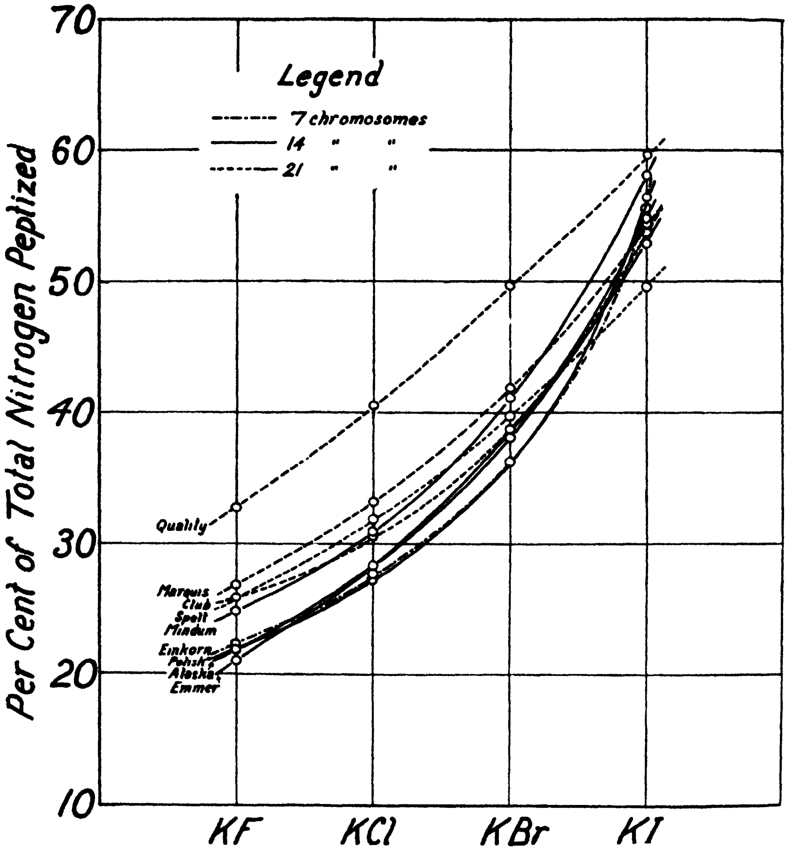

Fig. 1

Peptization of the Proteins of Various Triticum Species by 0.5 molar salt solutions.

The variation in the percentage of total nitrogen occurring in barley, oats, and wheat does not, apparently, account for the differences described above nor for the relative amounts of total nitrogen peptized. Oats contained the smallest amount of total nitrogen (1.859%) yet, with the exception of the *T. vulgare* group of wheats, a larger percentage of it was peptized than was true of either barley or the average for all of the *Triticum* species.

Peptization of the Proteins of Wheat.—In Table III and Fig. 1 are recorded the data obtained by peptizing the proteins of a number of wheats, most of which represent a distinct type. The fifth column of the table shows the percentage of the total nitrogen peptized by distilled water and was included for comparison with the amounts peptized by the various salts. Here again we have a marked lyotropic effect of the order $F < SO_4 < Cl < Br < I$. There is not a single reversal of this arrangement, although 10 different varieties of wheats were studied and 5 different salts employed.

If the peptization with one salt is compared with the peptization of another, proceeding from left to right across the table, it will be found that in a general way these differences are relative differences. These values have been recorded in Table IV. The differences as tabulated were obtained by subtracting the salt which peptized the least amount of nitrogen from the next one above it which peptized a larger amount. In Column 6 appear the figures found by subtracting the data for KF from that of KI. In this manner the differences are all positive. The last row of figures at the bottom of the table record the average differences between the various groups of salts. It is thus seen that there is less average difference between the peptization by K_2SO_4 and KF, than between KCl and K_2SO_4. The greatest variance is found, as one would expect, between KI and KF.

The data support the conclusion that considering all the wheats as a whole, their peptization behavior is very similar. Fig. 1 shows that while this statement is true generally, there are some differences. It will be seen that the grains divide themselves into three specific groups. The lower group includes White Polish, Emmer, Einkorn, and Alaska; the middle group comprises the varieties Spelt, Club, Durum, and Marquis, and the upper contains only one variety, Quality. This division, with the exception of Quality, is only true, however, with reference to the behavior of these grains toward the salts, KF and KCl. When the KBr level has been reached these differences have largely disappeared and nothing of this nature is observed when the peptization with KI is considered. In fact most of the lines have crossed one another.

It was thought that the division of the wheats into three groups might correspond to the classification of those grains which is sometimes made on the basis of their chromosome number. Sax[50] in confirmation of the studies of Sakamura[51] and Kihara[52] list the haploid numbers of the wheat group as follows:

Triticum monococcum	Einkorn group	7 chromosomes
T. dicoccum	Emmer group	14 chromosomes
T. durum		
T. turgidum		
T. polonicum		
T. spelta	Spelt group	21 chromosomes
T. vulgare		
T. compactum		

Reference to the graph will show that the grains are not thus divided on the basis of protein peptizability. It is to be noted, however, that three wheats of the Emmer group, *i.e.*, *T. dicoccum*, *T. turgidum*, and *T. polonicum* are found in the lower division. Einkorn is also found there, whereas if a strict subdivision were maintained on the basis of the chromosome number, it should form a group by itself. *T. durum*, theoretically, should belong to the Emmer group. However, it shows the peptization behavior of the Spelt wheats.

With the exception of *T. durum*, the Spelt group corresponds to the classification made on the basis of chromosome number. It must be borne in mind that Quality is a soft wheat. Had a number of wheats of this nature been included in the study, the gap between Quality and the Spelt wheats might not have been so apparent.

The average results for the entire group or for the *T. vulgare* varieties are higher than those reported by Gortner, Hoffman, and Sinclair.[45] This might have been expected, since our results were based upon the peptization of the proteins from the kernel, while theirs included only the proteins from wheat flour. Our results are likewise higher than those reported by Pascoe, Gortner, and Sherwood[46] who extracted various flour streams with 0.5 M salt solutions. It is interesting to note, however, that as the values given by them for the lower grades of flour are approached there is in general an increase in the percentage of the total nitrogen peptized. However, these values are much lower than the average we have obtained from whole wheat meal, the same salt being considered.

Peptization of the Proteins of Legumes.—The results obtained from peptizing the seed meals of various legumes are shown in Table I and Fig. 2.

Again we have evidence of a lyotropic series, the order of the anions being as follows: alfalfa, peanuts, and vetch, $F < Cl < SO_4 < Br < I$; beans, $F < SO_4 < Cl < Br < I$; clover, $F < Cl < Br < SO_4 < I$; peas, $SO_4 < Cl < F < Br < I$. This order is not as consistent as was found for the cereal grains. The discrepancy, however, is largely due to the potassium sulfate, the position of which varies from seed to seed. If this salt is omitted, the halogen salts assume the same order as before: $KF < KCl < KBr < KI$. There is only one exception to this arrangement and that is in the case of the pea, where the order of the fluoride and chloride anions is reversed. Table I shows that KF peptized 85.23% of total nitrogen, while KCl peptized 84.05%. It was thought that the value for KF might have been too high, but four different subsequent determinations of this value gave results which checked within experimental error of that percentage.

A much larger percentage of the total nitrogen of the legumes is peptized than is the case with the cereal grains. In fact the lowest value for KF in the case of the legumes is almost as high as the KI value for any cereal. This may be partially accounted for by the large amount of total nitrogen found in the legumes as contrasted with the smaller amount contained in the cereals.

The peptization range, together with the resulting difference between the peptization by the salt having the lowest value and that having the highest, is shown in Table XI. In the case of the pea if the value for KF instead of K_2SO_4 is taken as the minimal per cent, the difference becomes 9.96% instead of 11.24%. In so far as these differences are concerned the legumes divide themselves into two groups; beans, peas, and vetch form one, while alfalfa, clover, and peanuts form the other group.

TABLE XI

Showing the Maximum, Minimum, and Difference in the Percentage of the Total Nitrogen of the Legume Seed Meal peptized by Salt Solutions

Seed used	Minimum %	Maximum %	Difference %
Alfalfa	49.68	73.69	24.01
Beans	82.41	90.61	8.20
Clover	53.82	76.22	22.40
Peanuts	65.98	93.19	27.21
Peas	83.94	95.18	11.24
Vetch	70.66	77.96	7.30

The relationships between the various legumes are illustrated more clearly in Fig. 2. The curves for the pea and bean are quite similar and occupy about the same position in the graph. Alfalfa and clover are likewise similarly placed, but the curve for alfalfa is practically the reverse of that for clover. Vetch occupies a midway position. So far as the shape of the curves are concerned, it will be noted that the curves for pea, bean, vetch, and clover bear a resemblance to one another. Alfalfa and peanut have curves which are practically the reverse of those just mentioned but which, when compared with one another, are found to be of the same general character.

Peptization of the Proteins of Cruciferae.—The *Cruciferae* studied included the mustard, radish, and rape seeds. The data appear in Table I and in Fig. 2.

As in the legumes these seeds are characterized by the ready peptization of a high percentage of the total nitrogen. The lyotropic order of anions is mustard, $F < I < SO_4 < Br < Cl$; radish and rape, $F < SO_4 < Cl < Br < I$.

Mustard shows a marked difference in lyotropic behavior when compared with the radish and rape seeds. KI, which normally peptized a larger percentage of the total nitrogen than either of the other salts, peptizes practically the same amount of total nitrogen as KF. The iodide ion does not always occupy a paramount position in the lyotropic series. Fischer,[53] for example, using a number of salts, found the order of acid radicals bringing about a diminution in the swelling of fibrin in any acid or alkali to be $Cl < Br < NO_3 < CNS < I <$ acetate $< SO_4 <$ phosphate $<$ tartrate $<$ citrate. The sulfate ion in this case had a greater effect than did the iodide ion.

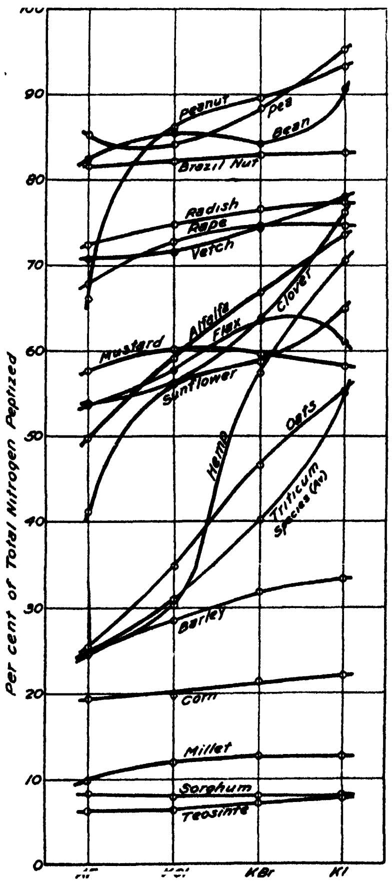

FIG. 2
A Composite Graph showing the Peptization of the Proteins of Various Seeds and Grains by 0.5 M. Salt Solutions

The peptization range of the *Cruciferae* is comparatively narrow, mustard ranging from 57.56 to 60.05% with a difference of only 2.49%; radish ranging from 72.36 to 77.43% with a difference of only 5.07%, and rape ranging from 67.71 to 74.61% with a difference of only 6.90%. The small differences in peptization behavior sharply distinguish the proteins of the *Cruciferae* from those of the other seeds thus far considered.

The curves for radish and rape are seen to be rather sharply differentiated from that of mustard, a much higher percentage of the total protein of the former seeds being peptized. The two curves are similar in nature which seems to indicate that the proteins of radish and rape have responded in an analogous manner to the action of the various salt solutions.

Peptization of the Proteins of Miscellaneous Seeds.—The seeds appearing under this title have been classified into two groups. The first four, yellow dent corn, white Ural millet, sweet sorghum, and teosinte, are in reality cereals and fall rather naturally into a group by themselves. Brazil nut, flax, hemp, and Russian sunflower make up the second group. The first four seeds will be designated collectively for the purpose of the present discussion as the "corn group."

(a) *The Corn Group.*—In many ways the "corn group" of seeds is the most interesting that has thus far been discussed. The entire group is characterized by having a very low percentage of peptizable protein. None of the other seeds or grains which have been studied in this laboratory even approach these low values. It is also noteworthy that the variation between the effect of the different salt solutions when a single seed variety is considered is in most cases of very small magnitude. It is obvious that in this group we are dealing with proteins having properties of an entirely different nature than was found, for example, in the case of the proteins of the other cereal grains.

If we list the anions in order of their lyotropic effect, the following series are found for the different members of the corn group: yellow dent corn and teosinte, $F < Cl < SO_4 < Br < I$; white Ural millet, $F < SO_4 < Cl < Br < I$; sweet sorghum, $SO_4 < Cl < Br < I < F$. *Actually*, however, these orders do not give the true picture, since the values for a number of the salts, considering a given seed variety, lie within experimental error of one another. Thus the percentages of the total protein of corn peptized are practically the same regardless of whether KF, K_2SO_4, or KCl solutions are employed. The lyotropic order accordingly would be more correctly indicated as $F, SO_4, Cl < Br < I$. In the case of millet, the salts, K_2SO_4 and KCl, have equal peptizing power, as have also KBr and KI; therefore, for this seed $F < SO_4, Cl < Br, I$. When the data for sorghum seed are considered, it is apparent that no lyotropic series exists. The same value is obtained in all cases, regardless of whether KF, K_2SO_4, KCl, KBr, or KI are used as the peptizing agent.

KF, K_2SO_4, and KCl peptize about the same percentage of the total nitrogen of teosinte, while KBr and KI peptize larger amounts; therefore, $F, Cl, SO_4 < Br < I$.

A graphical representation of the data for corn, millet, sorghum, and teosinte is included in Fig. 2. With the exception of millet, straight lines have been drawn connecting the points. The line for corn is separated from the other lines or curves, inasmuch as a higher percentage of its total nitrogen was peptized than was true of other members of the group. While teosinte and corn differ in the relative amounts of nitrogen peptized, yet it will be observed that the lines slope in the same direction. However, the angles which these lines make with the horizontal are not the same, the angle being greater in the case of corn.

(b) *The Proteins of Other Seeds.*—The peptization data for the second group of miscellaneous meals are also found in Table I and illustrated graphically in Fig. 2. The lyotropic series found for each of these seeds are Brazil nut and hemp, $F < Cl < SO_4 < Br < I$; flax, $F < Cl < I < Br < SO_4$; and sunflower, $F < SO_4 < Cl < Br < I$.

The percentage of the total protein peptized ranges from 81.58 to 83.19 with a difference of only 1.61% in the case of the Brazil nut; from 53.53 to 65.26 with a difference of 11.73% in the case of flax; from 41.18 to 64.90 with a difference of 23.72% in the case of sunflower, to 24.65 to 70.58 with a difference of 45.93% in the hemp seed meal.

The proteins of the Brazil nut are very easily peptized and resemble in this respect the proteins of the pea. With the exception of the position of the sulfate ion, the lyotropic series resembles that found for the cereal grains.

The peptization range, however, is much smaller, a difference of only 1.82% being found between KF and KI. Fig. 2 shows that a straight line can be drawn connecting all the points.

A very peculiar arrangement of the ions is found in the case of the flax-seed meal. While the fluoride solution peptizes the smallest quantity of protein, the sulfate instead of the iodide ion peptizes the largest amount. Perhaps the presence of gums or mucilages (typical lyophilic colloids) in the flax seed mask in some way the real lyotropic effect on the protein complex.

The data for hemp seed show that the sulfate solution peptizes approximately 16% more protein than does the chloride solution. However, the halogens follow the normal order. Hemp seed is especially interesting because of its great peptization range. KF only peptizes 24.65% of the total nitrogen, while KI extracts 70.56%. This difference of nearly 46% represents the greatest extreme of any of the seeds studied.

The sunflower seed has exactly the same lyotropic order of ions as was found for the cereals. The range in the percentage of total nitrogen peptized is also of the same order of magnitude as was found for oats and wheat.

The Albumin and "Globulin" Fractions of the Cereals.—Under the conditions of the experiment, water peptizes 15.12% of the total nitrogen of barley. Of this amount 3.74% is soluble in water and probably represents to a large extent the albumin fraction. The remainder, 11.38% may represent "globulins." Column (C) of Table II shows that following three water extractions, three extractions of the residue with 0.5 M KCl will dissolve an additional 7.05% of the total nitrogen. This added to the "globulin" presumably peptized by virtue of the salts originally present in the seed, gives a total of 18.43%. Thus, "globulins" amounting to 18.43% of the total nitrogen content were peptized by the combined effect of water and salt. To this we must add 3.74% to obtain the total amount of "globulin" and albumin peptized. The figures appearing in Column (G), Table II, were taken from the peptization experiments and show the percentage of total nitrogen peptized, using a KCl solution alone (no previous water extraction). Providing the protein was not denatured by water during extraction, the results given in Column (F) should be expected to check closely with those of Column (G). Column (H), which represents the difference between Columns (F) and (G) is a measure of the extent to which the protein was denatured by water previous to peptizing the meal residue with KCl. It is seen that 6.33% of the total protein of barley was denatured by water and was thus not peptizable by subsequent treatment with KCl solution.

While water extracts from oats but little more of the total nitrogen than it does from barley, nevertheless only 1.73% of the total nitrogen is water soluble as compared to 3.74% in barley. The apparent percentage of "globulin" is thereby increased. Two separate sets of figures appear for oats in Columns (C), (E), (F), (G), and (H). The top number in Column (C) shows the percentage of the total nitrogen peptized by an M/2 solution of KCl from the residue remaining after three extractions had previously been made with water. The lower figure indicates the percentage of the total nitrogen extracted by an M/2 solution of KBr following three water extractions. KBr, as would be expected, extracts a larger percentage of the total nitrogen than does KCl.

Osborne[9] found the proteins of oats to be rather easily denatured by dialysis. This conclusion is substantiated by Column (H), Table II. It is seen that 11.38% of the total nitrogen of oats was rendered non-peptizable by KCl and 20.59% by KBr, following a previous water extraction.

The data recorded in Table II for wheat (average) represent the average of all the results obtained from the various varieties and types of wheat, and were taken from Table V. It is included in Table II for purposes of comparison. The water-soluble fraction following dialysis is larger than for either oats or barley, although the per cent of "globulin" peptized is about the same as that for oats. Column (H) shows that the proteins of wheat are not so easily denatured by water as are those of barley or oats.

Table V contains the albumin-"globulin" data from a study made of a number of different types and varieties of wheats. The percentage of the total nitrogen peptized by water varies from 16.67% to 24.94%. The common wheats, Marquis and Quality, have 21.21 and 24.94%, respectively, of the total nitrogen which is peptized by water. Considerable variability is seen in the percentage of total water-soluble nitrogen. This ranges from Einkorn with 2.77% to Marquis with 7.04%. The "globulin" fraction remains fairly constant at 13 to 15% of the total nitrogen except for Spelt and Quality where values of 19.23% and 21.16% were found

The rather unusual behavior of Quality toward salt solutions is indicated in Fig. 1. The data of Table V show that it likewise ranks much higher in "albumin" and "globulin" nitrogen than any of the other cereals. This fact alone may account for the unique position occupied by this cereal in Table III and Fig. 1. However, in addition to Quality containing more albumin and "globulin," it is probable that its other proteins are more easily peptized by the salt solutions than is the case for the other wheats.

Column (H) of Table V is calculated in the same manner as the corresponding column in Table II and may be considered as an index of the degree to which the proteins of these cereals are denatured by water. It will be observed that the proteins of Alaska, Einkorn, and Emmer, are not easily denatured. Those of Little Club, White Polish, and Spelt are intermediate. The proteins of Mindum and the *T. vulgare* group, however, are more easily denatured, an average difference of about 3% being found between Columns (F) and (G).

The Albumin and "Globulin" Fractions of the Legumes.—The legumes (Table II) vary from 25.16 to 78.87% in the percentage of the total nitrogen extracted by water, the former figure representing Alsike clover and the latter Andes pea.

It is the opinion of most investigators that legume seeds contain large amounts of stored albumin. However, the term "albumin" seems to have had different interpretations placed upon it and has been rather loosely used. The generally accepted definition of an albumin is that of "a simple protein soluble in water and dilute salt solutions and coagulable by heat." Mann[54] however states that, "most of the vegetable albumins are globulins, *i.e.*, acid-albumins which are insoluble in pure water, but soluble in salt-solutions, and precipitable by dilution and acidification."

If we accept the present general opinion that albumins are proteins soluble in pure water, then our results as given in Column (B), Table II, do not substantiate the belief that legume seeds contain large amounts of albumin. It will be seen that navy beans contain only 14.11% of water-soluble nitrogen which is the largest amount found for any legume. Alfalfa seed contains only 3.29%.

Jones et al[22] isolated 1.75% of an albumin from the Lima bean. Only traces of an albumin were found by Johns and Waterman[23] in the Mung bean. Osborne and Campbell[24] found the legumin content of the pea to be 4%, lentil 10%, vetch 2.5%, and the horse bean 16% based on the weight of the meal used. On the other hand, Johns and Jones[29] found but a very small quantity of albumin in the peanut. These data indicate a considerable variation in the albumin content of legumes, just as we have shown in Table II. Osborne and Campbell found about twice as much legumin in the pea as in the vetch. Our figures show somewhat roughly the same relationship. In the case of peanut, however, we find 5.36% of the total nitrogen to be water-soluble, whereas Johns and Jones found but a very small quantity. A strict comparison, however, is hardly justified because of the difference in methods used and possibly differences in the samples employed for investigation, but it does indicate the need for further quantitative work on the proteins of the legumes.

Table II shows that the "globulin" fractions of the legumes differ considerably. The "globulins" extractable by water from Alsike clover meal amount to 21.74% of the total nitrogen, and from the pea meal to 68.01%. The total globulin content of these seeds as recorded in Column (E) gives clover 35.79% and peas 78.10%. In this respect alfalfa and clover resemble each other, whereas the bean and pea are grouped together at the other extreme.

Some very interesting relationships may be seen in Column (C). Peptization of the alfalfa meal residue with KCl solution following the water extractions peptizes only 8.52% of the total nitrogen. On the other hand, under the same conditions, 35.62% of the total nitrogen of the vetch seed is peptized. This amount is even greater than was peptized originally by water (25.48%). Water has a decided denaturing effect on the proteins of the legumes as may be seen by reference to Column (G), where a KCl solution peptized 71.48% of the total nitrogen, or over twice as much as was peptized by KCl following earlier water extractions.

That the legume "globulins" are denatured by water during dialysis is shown in Column (H). The proteins of the pea are less readily denatured than are those of the other leguminous seeds. The proteins of clover show the greatest denaturization effect.

It was found to be practically impossible to extract 6-gram samples of alfalfa and clover meals with 50 cc. of KCl solution. The presence of gums made it impossible to sediment the residual meal. Accordingly the percentages obtained by peptizing 0.5 gram portions of these meals have been inserted in the table in order that a comparative study might still be made in spite of the possibility that the difference in the size of the sample may have influenced to some extent the percentage peptized, and that the values appearing for alfalfa and clover in Columns (F) and (G) may not, for that reason, be strictly comparable with the figures for the other meals.

The Albumin and "Globulin" Fractions of the Cruciferae.—Only rape and radish seed meals were included in this phase of the problem. Water peptizes about the same percentage of the total nitrogen from both of these seed meals. They differ, however, in the percentage of the total nitrogen appearing as albumins. Column (B) shows that 8.46% of the total nitrogen of the radish seed peptized by water may be true albumin, whereas with rape the corresponding figure is 12.37%.

The Albumin and "Globulin" Fractions of the Corn Group.—These seeds form an isolated group of Table II when the various nitrogen fractions are considered. Only from 4.98 to 12.58% of the total nitrogen is extractable by water. These are the lowest values for any group of seeds studied. Of the four seeds, corn ranks highest in this respect and teosinte lowest. These seeds stand in Table II in almost the same relative order as they did when compared upon the basis of the percentage of their total nitrogen which was salt-soluble (Table I). Millet is an exception, however, and does not yield its nitrogen so readily to water as does sorghum seed.

Considerable difference between the four seeds is noticed when they are compared on the basis of the percentage of total nitrogen appearing in the albumin fraction. In this respect sorghum and teosinte have identical amounts (0.83%), with millet 1.43%, and corn 3.34%.

In percentage of total "globulin" the members of this group stand in exactly the same order as they did in Table I. It should be noted that the "globulin" content of corn is from twice to three times that of millet, sorghum, and teosinte, respectively. These seeds are also outstanding when their stability toward water is considered. The proteins of corn, sorghum, and teosinte are very stable, while the proteins of millet undergo some denaturation.

The Albumin and "Globulin" Fractions of Other Miscellaneous Seeds.—These seeds include the Brazil nut, flax, hemp, and Russian sunflower.

Brazil nut resembles vetch in that the salt extraction of the residue from the water extraction dissolved more nitrogen than was peptized by the water previous to treatment by KCl solution. Flax has 64.07% of the total nitrogen peptizable by water, of which 15.64% is albumin. Attention is called to Column (H), Table II, where a negative value of 16.81% is recorded. In the discussion of Table I we noted that the presence of gums in flax meal undoubtedly masked the lyotropic effect which might have been obtained had the gums not been present. The value of 57.64% which appear in Column (G) is, for that reason, probably too low. The figure given in Column (H), therefore, probably reflects in some manner the effect of the presence of gums upon the peptization behavior of the flax proteins.

The Effect of Different Reagents on the Total Nitrogen peptized, using the Same Charge of Sample.—Following the water and KCl peptization of a number of the samples listed in Table II, it was decided to re-extract the residues in the same manner, using 0.5 M KBr solution. No attempt was made to remove the small amount of KCl held by the moist residue before adding the KBr solution. The data are recorded in Table VI.

It will be seen that following the extractions by water and KCl, the addition of a 0.5 M KBr solution to the residue of barley peptized an additional 3.38% of the total nitrogen. The total amount extracted by water, KCl, and KBr was 25.55% of the total nitrogen. Column 6 shows that the water peptized 2.14 times as much of the total nitrogen of barley meal as did KCl following the water extraction. Column 7 indicates that KCl extracted 2.09 times as much nitrogen as did the subsequent extraction with KBr. Similarly 4.47 times as much nitrogen was extracted by water as was peptized by KBr following extraction by KCl.

An interesting relationship will be noted in the case of oats. Two samples of this meal were first extracted with water, 16.77% of the total nitrogen being peptized in the one case and 16.81% in the other. From this point on, the procedure was varied. Sample (1) was further extracted with KCl, followed by KBr. Sample (2) was further extracted with KBr followed by KCl. Column 5 shows that it makes little difference which salt directly follows the water extraction, since the total nitrogen extracted by water, KCl, and KBr totals about the same in either instance.

"Globulin"/Albumin Ratios from the Water Extracts.—The last columns of Tables II and V show the "globulin"/albumin ratios as obtained from all of the seeds studied. It will be observed that no two of the ratios are exactly alike. Even the cereal grains, which might have been expected to have had similar ratios, vary widely.

"Globulin"/Albumin Ratios from the Salt Extracts.—We have already suggested that the particular method employed in estimating the albumin and "globulin" fractions seemed to determine very largely the ratios found by other workers between these two proteins. In order to test this point further it was decided to make a number of salt extractions in exactly the same manner as was employed in the instance of the water extracts. The samples chosen for the study were corn, millet, sorghum, teosinte, and Brazil nuts. The results are shown in Table VII. Column 5 gives the ratios as computed from the salt extracts and Column 6 contains the ratios found from the water extracts. The disagreement between the two sets of values is most striking. Since exactly the same procedure was employed in both cases except that a different solvent was used, one must conclude that these differences are the result of employing two different methods. We feel justified, therefore, in concluding that our results substantiate what has been found by others, although never sufficiently emphasized, *i.e.* that the technic which is em-

ployed will determine to a large extent the ratio which one may expect to find between the globulin and albumin fractions of a seed. As to which method should be used of the many that might be considered, no data are at present available.

Does Elimination of the Ether-Extractable Material from a Seed Increase the Percentage of Peptizable Nitrogen?—This study included four legumes, beans, peas, alfalfa, and clover, together with hemp and corn. The percentage of ether extract ranged from 0.61% for the hemp meal which had previously been partially extracted with gasoline, to 11.72%. The data are shown in Table X.

It will be noted that with the exception of the alfalfa meal a greater percentage of the total nitrogen was peptized from the fat-free meal than from the whole seed meal. To explain the differences noted, one has only to assume that a part of the proteins of the seed are imbedded in or surrounded by a layer of fat or fat-like substances. Such an imbedding would act to prevent the ions of the salt from coming in contact with the proteins and thus exerting their maximum peptizing effect.

Protein Classification and the Lyotropic Series.—Gortner, Hoffman, and Sinclair[45] were the first to object to a system of protein classification based upon "solubility." Regarding the globulin fraction, they definitely raised the question of what salts should be used and what concentrations. As a result of their studies on twelve different wheat flours and solutions of twenty-two different inorganic salts, they state:* "We do not believe that any salt used, in any one of the concentrations, extracts a chemical entity which should be designated by the term 'globulin.' Our experiments would indicate that all of the various protein fractions (with the exception of the proteose) which have been considered fixed entities, and characteristic of wheat flours are, if we follow the prescribed routine procedure for protein isolation, capable of realization, but that, if the routine procedure is somewhat altered, fractions having different properties and characteristics are obtained." The recent work of Pascoe, Gortner, and Sherwood,[46] and Sinclair,[49] as well as the data reported in this paper have added confirmatory evidence to the findings of Gortner, Hoffman, and Sinclair.

Perhaps certain seeds or plant tissues may contain true chemical entities which can be designated as globulins. The peptization behavior of our Brazil nut meal indicates that a true globulin may be present in that seed and there are probabilities that the same may be true for radish, rape, and mustard seeds. It may be that only "crystalline" globulins are chemical entities and that the amorphous globulin preparations recorded in the literature are non-homogeneous fractions whose chemical and physical properties depend upon the technic employed in their isolation. However, the peptization behavior of the hemp seed meal certainly raises the question as to which salt solution isolates the chemical entity, "crystalline edestin;" which question can only be answered by further investigations.

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* It should perhaps be emphasized that their statement has particular reference to the proteins of the wheat endosperm.

Many years ago Ritthausen questioned the homogeneity of the albumin fraction as prepared from vegetable seeds. He suggested that the substance coagulated by boiling the aqueous extract of seed meals might belong to other groups of proteins which had to some extent been "dissolved" in the water. The protein literature to date renders questionable the existence in seeds of a true albumin with constant physical and chemical properties, such as characterize egg albumin. Therefore the preceding discussion of the varying albumin:globulin ratios with varying technic applies with equal force either to the "albumin" or the "globulin" fraction.

Only recently Blish and Sandstedt[55] have questioned the chemical individuality of the protein, glutenin, of wheat. They note that boiling 70% alcohol peptized glutenin and that six successive extractions of 20 grams of supposedly "pure" glutenin, each with one liter of boiling 70% alcohol peptized a total of 25.9% of the glutenin. Even after these six successive extractions more of the residue could be peptized by further extraction. However, the most striking feature of their work lies in the fact that *the composition (as expressed by a Van Slyke analysis) of the protein peptized varied from extract to extract* and also from the Van Slyke analysis of the original glutenin. They conclude: "It appears more than likely that 'glutenin,' as ordinarily prepared by the use of dilute alkali, is not a naturally occurring individual protein, but merely a 'fraction' derived through the action of the alkali, and varying somewhat in composition according to the strength of the alkali used, as well as with the time and temperature of extraction."

Glutenin has been regarded by workers in the field of the vegetable proteins as one of the most completely studied and characterized of the plant proteins. Osborne undoubtedly regarded it as a chemical entity so that in the light of the observations of Blish and Sandstedt, Osborne's[48] (p. 13) statement, "We can, therefore, for the present, treat as individual proteins only those products whose extensive fractionation has given no evidence that a mixture is being dealt with, and we must await new methods of study before any one of these proteins can be definitely accepted as a true chemical entity. Many, however, of the proteins with which we are at present familiar have shown such constancy of composition and properties that we feel justified in now considering them as substances of reasonably definite character," becomes doubly significant.

The above discussion has been directed primarily at the problems facing the worker in the field of the vegetable proteins. Whether or not they apply with equal force to the "proteins" isolated from animal fluids, cells, and tissues can only be answered by studies in which the animal fluids or tissues are peptized under a variety of conditions. However, the recent observations of Lustig[56] appear to be significant. Using non-standard technic Lustig isolates from blood serum three euglobulins, two pseudoglobulins, and three albumins! These preparations differed sharply from each other in both physical and chemical properties. If Lustig's fractions represent chemical entities, then the earlier preparations of the serum proteins were non-homogeneous. But there is no evidence that Lustig's preparations cannot be further fractionated by other technics. The whole question of protein individuality, protein classification, and protein isolation needs to be critically studied, and the workers in this field should divorce themselves from all preconceived notions as to what constitutes orthodox or non-orthodox technics.

Abderhalden[57] has drawn attention to the fact that the proteins as we work with them in the laboratory are not in the same physical state as they were originally in the cell. In fact the significant role they are called upon to play in vital phenomena depends upon their easy convertibility and sensitivity. He states that certain of the proteins in protoplasm undoubtedly have properties that are still unknown to us.

If Abderhalden is correct, then a number of the nitrogen-containing preparations which we term proteins may not in reality be distinct entities, but may be simply fractions of a large structure of which we know very little. From this viewpoint chemical reagents may, in many instances, merely bring about the peptization of a larger micelle into certain of its component parts, the properties and composition of which are determined by the reagent and technic which were used. Thus in the peptization of proteins by water, salt solutions, dilute alcohol, dilute alkali, etc., it may be that we are only fractionating a single primary substance and by changing to other reagents (*e.g.*, other salt solutions) another series of different fractions of this same primary substance may be obtained.

Summary

A study has been made of the peptizing effect of M/2 aqueous solutions of certain inorganic salts on the proteins of twenty-eight different seeds and grains. The investigation included barley, oats, and wheat, six different legumes, three *Cruciferae*, and other miscellaneous seeds. At least one variety of each of the eight principal types of wheats was investigated.

The data as presented seem to warrant the following conclusions:

1. A definite lyotropic or Hofmeister series of anions has been observed as influencing the peptization behavior of most of the seed protein complexes.

2. Barley, oats, and all of the varieties and types of wheats studied have the same lyotropic series, the anions arranging themselves in the order of increasing peptization effect of $F < SO_4 < Cl < Br < I$. Some variation is found in the case of the legume seeds. If the halogens alone are arranged, the order is essentially $F < Cl < Br < I$. The lyotropic order for the pea, however, is $SO_4 < Cl < F < Br < I$. Of the *Cruciferae*, radish and rape meals have the lyotropic order of anions of $F < SO_4 < Cl < Br < I$; mustard meal, $F < I < SO_4 < Br < Cl$.

3. The lyotropic effect in the case of corn, millet, sorghum, and teosinte meals is much less pronounced than that found for the other seeds. In fact no lyotropic order of anions could be demonstrated for sorghum seed.

4. Brazil nut meal and hemp meal had a lyotropic order of anions of $F < Cl < SO_4 < Br < I$; flax meal, $F < Cl < I < Br < SO_4$; and sunflower meal, $F < SO_4 < Cl < Br < I$.

5. The peptization behavior of the various groups of related seeds appears to be rather distinct and characteristic of each group.

6. Although the same methods were employed in each case, different globulin: albumin ratios were found where extractions were made with distilled water followed by 0.5 M KCl and those where only 0.5 M KCl was used.

7. A greater percentage of the total nitrogen was extracted from fat-free meals than from the whole grain meals.

In conclusion it is emphasized that protein "solubility" is in reality protein peptization, and that the technic which is employed may largely determine the yield and the properties of the protein complex which is isolated. The existence of true plant "albumins" as definitely characterized chemical entities is questioned. The available evidence indicates that many of the preparations which have hitherto been regarded as homogeneous and distinct plant proteins may in reality either be heterogeneous mixtures or else merely fragments of a larger and more complex protein micelle.

Literature cited

[1] Denis, P. S.
1859. Mémoire sur le sang considéré quand il est fluide, pendant qu'il se coagule et lorsqu'il est coagulé, suivi d'une notice sur l'application de la méthode d'experimentation par les sels à l'étude des substances albuminoides; mémoire presenté a l'academie des sciences le 20 décembre, 1858, viii, 208 pp. Paris, J. B. Baillière et fils (Quoted by Osborne 48, p. 21).

[2] Hoppe-Seyler, F.
1866-71. "Ueber das Vitellin, Ichthin und ihre Beziehung zu den Eiweissstoffen, Medicinisch-chemische Untersuchungen," p. 215-220.

[3] Weyl, Th.
1877. Beiträge zur Kenntniss thierischer und pflanzlicher Eiweisskörper, Z. physiol. Chem., **1**, 72-100.

[4] Vines, S. H.
1879-80. On the Chemical Composition of Aleurone Grains, Proc. Roy. Soc., **28**, 218-221; **30**, 387-393.

[5] Osborne, T. B.
1895. The Proteids of Barley, J. Am. Chem. Soc., **17**, 539-567.

[6] Bishop, L. R.
1929. Composition and Quantitative Estimation of the Barley Proteins. II, J. Inst. Brewing, **35**, 316-322.

[7] Norton, J. P.
1848. Account of Some Researches on the Protein Bodies of Peas and Almonds, and a Body of somewhat Similar Nature existing in Oats, Am. J. Sci., **5**, 22-33.

[8] Bibra, Von.
1860. "Die Getreidearten und das Brod," VIII, 502 (Quoted by Osborne 9).

[9] Osborne, T. B.
1891-92. The Proteids or Albuminoids of the Oat Kernel, Am. Chem. J., **13**, 327-347; 385-413; **14**, 212-224.

[10] Osborne, T. B.
1907. Proteins of the Wheat Kernel, Carnegie Institution of Washington, Publication No. 84.

[11] Ladd, E. F.
1909. Report on Cereal Products, U. S. D. A. Bur. Chem., Bull. 122: 53-58.

[12] Jones, D. B., and Gersdorff, C. E. F.
1923. Proteins of Wheat Bran. I. Isolation and Elementary Analysis of a Globulin, Albumin, and Prolamine, J. Biol. Chem., **58**, 117-131.

[13] Bailey, C. H., and Blish, M. J.
1915. Concerning the Identity of the Proteins extracted from Wheat Flour by the Usual Solvents, J. Biol. Chem., **23**, 345-357.

[14] **Hoffman,** W. F., and Gortner, R. A.
1927. The Preparation and Analysis of the Various Proteins of Wheat Flour with Special Reference to the Globulin, Albumin, and Proteose Fractions, Cereal Chem., **4**, 221-229.

[15] **Gorham,** J.
1821. Analysis of Indian Corn, Quarterly J. Sci., **2**, 306-308.

[16] **Ritthausen,** H.
1872. "Die Eiweisskörper der Getreidearten, Hülsenfruchte und Oelsamen," XI, 252 s.

[17] **Chittenden,** R. H., and Osborne, T. B.
1891-92. A Study of the Proteids of the Corn or Maize Kernel, Am. Chem. J., **13**, 453-468, 529-552; **14**, 20-44.

[18] **Osborne,** T. B.
1897. The Amount and Properties of the Proteids of the Maize Kernel, J. Am. Chem. Soc., **19**, 525-532.

[19] **Osborne,** T. B.
1884. Ueber die Zuzammensetzung der mittelst Salzlösung dargestellten Eiweisskörper der Saubohnen (Vicia Faba) und weissen Bohnen (Phaseolus), J. prakt. Chem., (2) **29**, 448-456.

[20] **Osborne,** T. B.
1894. The Proteids of the Kidney Bean, J. Am. Chem. Soc., **16**, 633-643.

[21] **Osborne,** T. B., and Campbell, G. F.
1897. Proteids of the White Podded Adzuki Bean, J. Am. Chem. Soc., **19**, 509-513.

[22] **Jones,** D. B., Gersdorff, C. E. F., Johns, C. O., and Finks, A. J.
1922. Proteins of the Lima Bean, Phaseolus Lunatus, J. Biol. Chem., **53**, 231-240.

[23] **Johns,** C. O., and Waterman, H. C.
1920. Some Proteins from the Mung Bean, Phaseolus Aureus Roxburgh, J. Biol. Chem., **44**, 303-317.

[24] **Osborne,** T. B., and Campbell, G. F.
1898. The Proteids of the Pea, Lentil, Horse Bean, and Vetch, J. Am. Chem. Soc., **20**, 410-419; cf. also Proteids of the Vetch, J. Am. Chem. Soc., **20**, 406-410.

[25] **Osborne,** T. B., and Harris, Isaac F.
1907. The Proteins of the Pea (*Pisum Sativum*), J. Biol. Chem., **3**, 213-217.

[26] **Osborne,** T. B., and Campbell, G. F.
1896. Legumin and Other Proteids of the Pea and the Vetch, J. Am. Chem. Soc., **18**, 583-609.

[27] **Ritthausen,** H.
1880. Ueber die Eiweisskörper verschiedener Oelsamen, Pflüger's Archiv., **21**, 81-104;

[28] **Lechnikov,** I. S.
1913. Separation and Hydrolysis of Albuminous Substances from the Seeds of Arachis hypogea (Rec. Trav. Lab. Agron. 9: 378-385). Exp. Sta. Rec. **35**, 712.

[29] **Johns,** C. O., and Jones, D. Breese.
1916. The Proteins of the Peanut, Arachis Hypogaea. I. The Globulins, Arachin and Conarchin, J. Biol. Chem., **28**, 77-87.

[30] **Osborne,** T. B.
1892. Proteids of the Flax Seed, Am. Chem. J., **14**, 629-661.

[31] **Vines,** S. H.
1881. On the Proteid Substances Contained in the Seeds of Plants, J. Physiol., **3**, 93.

[32] **Osborne,** T. B., and Campbell, G. F.
1897. The Proteids of the Sunflower Seed, J. Am. Chem. Soc., **19**, 487-494.

[33] **Johns,** C. O., and Chernoff, L. H.
1918. The Globulin of Buckwheat, Fagopyrum Fagopyrum, J. Biol. Chem., **34**, 439-445.

[34] **Jones,** D. B., and Johns, Carl O.
1916. Some Proteins from the Jack Bean, Canavalia Ensiformis, J. Biol. Chem., **28**, 67-75.

[35] **Johns,** C. O., Finks, A. J., and Gersdorff, C. E. F.
1919. Globulin of the Cocoanut, Cocos Nucifera. I. Preparation of Cocoanut Globulin. Distribution of the Basic Nitrogen in Cocoanut Globulin, J. Biol. Chem., **37**, 149-153.

[36] **Davies,** W. L.
1927. The Proteins of Green Forage Plants, J. Agr. Sci., **17**, 33-40.

[37] **Johns,** C. O., and Gersdorff, C. E. F.
1920. The Globulin of the Cohune Nut, Attalea Cohune, J. Biol. Chem., **45**, 57-67.

[38] Cajori, F. A.
1921. A Globulin as the Principal Protein of the Pecan Nut: Its Chemical and Nutritive Properties, Proc. Soc. Exp. Biol. Med., **19**, 52.

[39] Jones, D. B., and Gersdorff, C. E. F.
1923. Proteins of the Cantaloupe Seed, Cucumis melo, J. Biol. Chem. **56**, 79-96.

[40] Takahashi, Eiji, and Itagaki, Tadao.
1925. On the Proteins of the Adzuki-Bean (Adzukia subtrilobata), J. Biochem. (Japan), **5**, 311-319.

[41] Jaeger, F. M.
1917. Temperatur Abhängigheit der Molekuloren freien Oberflachenenergie von Flüssigkeiten im Temperaturbereich von −80 bis +1650°C., Z. anorg. allgem. Chem., **101**, 1-214.

[42] Frumkin, A.
1924. Potentialdifferenzen zwischen Flussigkeiten und Luft, Kolloid-Z., **35**, 340-342.

[43] Freundlich, H.
1926. "Colloid and Capillary Chemistry," 58.

[44] Loeb, J.
1921. Ion Series and the Physical Properties of Proteins. III. The Action of Salts in Low Concentration, J. Gen. Physiol., **3**, 391-414. *Cf.* also "Proteins and the Theory of Colloidal Behavior," 14-15 (1922).

[45] Gortner, R. A., Hoffman, W. F., and Sinclair, W. B.
1928. Physico-chemical Studies on Proteins. III. Proteins and the Lyotropic Series, Colloid Symposium Monograph, **5**, 179-198 *Cf.* also The Peptization of Wheat Flour Proteins by Inorganic Salt Solutions, Cereal Chem., **6**, 1-17 (1929).

[46] Pascoe, T. A., Gortner, R. A., and Sherwood, R. C.
1930. Some Comparisons between commercially and experimentally Milled Flours Cereal Chem., **7**, 195-221.

[47] Osborne, T. B , and Harris, I. F.
1905. The Solubility of Globulin in Salt Solution, Am. J. Physiol., **14**, 151-171.

[48] Osborne, T. B.
1924. "The Vegetable Proteins."

[49] Sinclair, W. B.
1929. The Effect of Inorganic Salt Solutions on Gliadin, Ph.D. thesis, University of Minnesota (Manuscript copy on file in the Library of the University of Minnesota).

[50] Sax, K.
1921. Chromosome Relationships in Wheat, Science, **54**, 413-415.

[51] Sakamura,
1918. Bot. Mag., Tokyo, Vol. 32 (Quoted by Sax, K. Chromosome Relationships in Wheat, Science, **54**, 413-415 (1921)).

[52] Kihara,
1919 and 1921. Bot. Mag., Tokyo, Vols. 33 and 35 (Quoted by Sax, K., Chromosome Relationships in Wheat, Science, **54**, 413-415 (1921)).

[53] Fischer, Martin H.
1915. "Oedema and Nephritis," 51.

[54] Mann, Gustav
1906. "The Chemistry of the Proteids."

[55] Blish, M. J., and Sandstedt, R. M.
1929. Concerning the Nature of the Protein extracted from Wheat Flour by Hot Alcohol, Cereal Chem., **6**, 494-503.

[56] Lustig, B.
1930. Zur Kenntnis der Unterfraktionen der Globuline und Albumine im Serum, Biochem. Z., **225**, 247-263.

[57] Abderhalden, E., and Komm, E.
1924. Über die Anhydridstruktur der Proteine, Z. physiol. Chem., **139**, 181-204.

THE COLLOID CHEMISTRY OF INSANITY. I*

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It is only natural that a subject as interesting as insanity should have attracted the thoughts of men from the earliest times and invited speculations concerning its cause. In ancient times there was a difference of opinion even among the "wise men." Western civilizations regarded the afflicted person as one possessed of the devil and treated him accordingly. On the other hand, Eastern religions reasoned that the supreme being had prematurely removed the patient's soul as a special mark of favor. Neither of these explanations satisfy the intellect, nor are they acceptable to the medical science. However, the difference of opinion still exists.

Medical research was not slow to realize that physical causes were often at the base of the trouble. Indeed their studies of the subject showing the relation of diseases, growths, drugs, and in some cases the absence or underdevelopment of certain structures warranted the belief that all types of this affliction might be traced to some definite physical cause, i.e., some abnormal variation in the structures of the nervous system.

A Meyerson[1] expresses the idea thus: "When we speak about the causes of the major mental disorders, we must leave out of account the psychoanalytic and psychological points of view. Neither Freud, Jung, or Adler, to mention the great triumvirate who, like their Roman predecessors, once were in amity and now hopelessly divided, have dealt in sufficient measure with the insanities to give their points of view a validity. Nor is what they have contributed on these matters at all pragmatically recognized in the practical world which deals with the mentally sick. Nor is the psychological point of view, e.g., of Bernard Hart, that mental diseases are psychological situations which must be psychologically studied and treated, anything more than a philosophical pronunciamentio. When a patient has had his skull crushed in and develops a delirium (which is, of course, a mental disorder), neither psychiatrist nor surgeon is fundamentally psychological either in his understanding or his treatment of the case. Physical in its cause, they employ physical means."

It is indeed disappointing to admit that the above point of view has not withstood the criticisms, and that in a number of cases there have been found no definite physical variations in the nervous system that would justify that viewpoint. Meyerson again formulates this delicate situation thus: "The term 'organic' in medicine means that some organ is involved in its structure in a way which can be studied satisfactorily after death by the post-mortem

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[1] "The Psychology of Mental Disorders" (1927).

examination, or which can be tested out chemically or microscopically in life. This term is in contrast with the term 'functional' which implies that no study during life or after death reveals changes in structure, though very evidently there is something wrong with the working (i.e. function) of a part."

It is not the intention of this paper to discuss either point of view and its relative virtues but rather to indicate the application of colloid chemistry to this problem. To some workers this may appear audacious, that colloid chemists should claim that some of the phenomena are colloid in nature. We do not insist that colloid chemistry will explain all of the phenomena or serve as an extensive basis; but it is not improbable that, when medical knowledge is supplemented with colloid chemistry, the medical research worker, in addition to enjoying the fruits of both medical and chemical knowledge, will be freed of some of the present difficulties in regard to the "functional" disorders.

Colloid chemistry is still a very young science and indeed owes much to biological workers for its discovery and early development. Its close relationship to biology and medicine is shown in the universal regularity: that all living matter is colloidal in nature. The colloidal nature of the proteins, polysaccharides, fats, lipoids, enzymes, glycogen, etc., is the essence of their importance to the living cell. In fact everything in the cell is either colloidal in nature or can cause the colloids to undergo some change.

Despite this clear-cut case it is a perpetual source of surprise to some that medical workers do not attempt the study of colloid chemistry and apply it to their investigations. This peculiar state of affairs is understandable however if one considers the nature of some of their problems. A large number of pathological conditions can be easily demonstrated and studied by "fixing" and staining sections of the tissue and examining them with an ordinary microscope Let us take a specific example that concerns the nature of this paper, the histology of the nervous system. In order to examine this tissue in the regular way it is "fixed" usually in alcohol or formaldehyde containing various chemicals such as: bichloride of mercury, nitric acid, zinc chloride, ammonium molybdate, gold salts, acetic anhydride, picric acid, iodine, iron alum, osmic acid, silver nitrate, oxalic acid, or chromium salts.[1] The material is dehydrated, by passage through absolute alcohol, then embedded in paraffin. The material can now be cut easily into thin sections and stained by various dyes after removing the paraffin with xylene. This is the normal procedure for all material requiring microscopical examination. Colloid chemists will immediately note that the above reagents are, without exception, violent coagulating agents. The material that has been treated with such violent agents has nothing in common with a normal cell except the name.

The reason for this procedure lies in the fact that, when microscopes with bright-field condensers are used, naturally objects whose refractive index is close to that of the surrounding medium cannot be seen clearly unless they are stained. The normal protein colloids do not have any appreciable tendency to adsorb dyes and become stained as long as they are peptized. In order to induce them to stain it is necessary to coagulate the material; hence the "fixing" agents are merely coagulating agents. The appearance of the finished preparation depends upon what fixing agent was used; naturally different types of coagulating agents produce different types of coagulation. It is interesting to note that when normal living cells are studied under the ultramicroscope they present an appearance radically different from that observed in the fixed and stained preparations.[1]

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[1] Lee: "The Microtomist's Vade-Mecum" (1928).

Still, this method can demonstrate bacteria in the tissues, the presence of abnormal growths, the absence of other structures, the extent of injury or degeneration, the differentiation of tissues, etc., so it has found a definite and valuable place in medicine. But it is indeed irrational to take the position that only knowledge gained through such methods is of any value to medicine, and that colloid chemistry is overstepping the bounds of propriety in pointing out that conclusions drawn from such studies are emphatically incomplete in relation to the living cell. For by their very nature they exclude the most characteristic properties of living material, namely the colloidal variations of the cell.

Insanity is a phenomenon exhibited by living beings and the fact that medicine has demonstrated only causative agents such as bacterial disease, presence of abnormal growths, the absence of other structures, and injury and degeneration causes no surprise to colloid chemists. It is a certainty that at least some types of mental disorders are due to the abormal variations of the colloids of the living nervous tissue. To what extent this may be generalized is not known at present but it cannot be excluded as a possible factor in any case not already explainable upon the basis of disease or organic disorders. Furthermore, since such variations are merely in degree of dispersion it will be impossible to observe these physical changes with modern histological methods because the basis of such technique depends upon complete coagulation before the material is ever examined.

Naturally, an interested worker would desire to know what would be the effects of a given variation in the degree of dispersion of the colloids of the nervous system, what variations are possible, and upon what evidence the conclusions have been based. The eminent pharmacologist, C. Binz,[2] and Cláude Bernard[3] "the father of physiology" pointed out that the reversible coagulation of the sensory nerves and brain would account for all of the phenomena of narcosis. This theory soon fell into disrepute for two reasons: the assumptions regarding the process of coagulation were regarded as improbable and secondly their contemporaries were unable to fully comprehend the colloidal nature of the theory. Recently the assumptions were reinvestigated and found to be correct.[4] For the sake of clearness the reversible coagulation mentioned above does not mean the degree of coagulation observed in eggs on boiling, or in milk on becoming acid, or in the clotting of blood. It is true that it is similar to these cases but it differs markedly in degree, the coagulation is very light: it cannot be seen with the naked eye and cannot be observed with an ordinary microscope. The flocculation can often be seen with the aid of an ultramicroscope and can be demonstrated in general by certain changes in the viscosity of the cell protoplasm.

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[1] G. Marinesco: Kolloid-Z., 11, 209 (1912); S. DeWitt Ludlum, Taft and Nugent: Archiv. Neurol. Psychiat., 23, 1121 (1930).

[2] Deutsche Klinik, Nr. 29, 277 (1860).

[3] "L'Anesthésie" Union Med., Paris, 8, 109 (1869).

[4] Bancroft and Richter: J. Phys. Chem., 35, 215 (1931).

By reversible coagulation is meant that the colloidal material returns to its normal state as soon as it is freed from the coagulating agent. This type of colloidal change in nervous tissue will inhibit its action and cause it to be in a state of narcosis. It is the "semi-coagulation" of Claude Bernard and can be brought about by certain drugs, suffocation, heat, cold, electrical currents, a physical blow, or even by the injection of water in some cases.[1] The first two agents are the most important from the biological point of view.

Various other explanations have been advanced to explain the action of drugs such as their distribution coefficients, surface tension, etc.; but the action of a drug does not depend so much on the physical properties of the substance as on the physical changes it initiates in the tissues. These changes are variations in the degree of dispersion of the colloids and this is the reason why intangible agencies as heat, cold, electricity, etc., can cause similar effects. The physical properties of a drug merely determine the distribution of the substance within the organism.

Suffocation can also bring about changes in the tissue colloids but in a roundabout fashion. Both aerobic and anaerobic oxidations not only serve as a source of energy to the cell but are very efficient detoxicating mechanisms. When asphyxiation is brought about, it allows the toxic products to accumulate to such a degree that they will cause the coagulation of the cell colloids. The following illustration may clarify the idea somewhat: most workers are familiar with the fact that a part of the lactic acid formed in certain tissues is converted back into glycogen and a part is oxidized to carbon dioxide and water. In the absence of oxygen the lactic acid accumulates to a marked extent. It is not so well known that lactic acid, or the lactates, can behave as narcotics. Nevertheless, it is an established fact.[2] The ability of lactic acid to coagulate bio-colloids is a familiar household experience in the souring of milk. One must bear in mind that there are a large number of substances that will accumulate and behave as in the above example, although the specific lactic acid example is used in the sense of an analogy rather than of an identity.

In connection with the phenomena of reversible coagulation it is interesting to note that the increasing instability of the colloids, before coagulation has taken place, is associated with the phenomena of stimulation. The stimulation is manifested in many forms depending upon the type of substrate which is affected, thus enzymes show greater activity, some cells show increased growth and activity, nerves an increased irritability, while in the brain tissue the stimulation is manifested by bizarre mental reactions as in drunkenness. Thus in passing into narcosis the tissue is first stimulated then narcotized; on recovery the passage back through the phase of stimulation is again noted. The increased activity of biological systems in their reactions and responses when the colloidal systems within them are approaching coagulation is quite important.

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[1] Bancroft and Richter: J. Phys. Chem., **35**, 215 (1931).

[2] E. Mendel: Deutsch. med. Wochenschr., Nr. 17 April 29, (1875); Moskowski Wratschevni Westnik, **1876** No. 7.

Another type of coagulation has been studied and its importance and application pointed out.[1] This type is the irreversible coagulation of the cell colloids. Whenever irreversible coagulation occurs within a cell the result is death, provided the coagulation is extensive. The reversibility depends to a large extent upon a time factor; as a rule the reversibility of the coagulation becomes increasingly difficult the longer it is allowed to stand. With disinfectants a dense, irreversible coagulation is produced and in a number of cases can be observed with the ultramicroscope. An antiseptic behaves towards bacteria as an anesthetic affects higher organisms. It inhibits the activity of the organism but does not kill unless the coagulation, due to the high concentration of the substance or the great length of time it is acting, becomes irreversible. The facts are briefly this: a coagulating agent first stimulates, inhibits, and then becomes lethal; the corresponding colloidal variations are: instability, reversible coagulation, and irreversible coagulation. If the substrate happens to be bacteria the order is the same: stimulation, antisepsis, and then disinfection. The phenomena and the colloid chemistry are the same on all simple substrates although the medical names vary. If we start with the assumption, that insanity is due to an abnormal state of dispersion of the brain colloids, we can have two types of insanity, one when the brain colloids are over-coagulated, and the other when the brain colloids are over-dispersed. The general changes on adding dispersing agents will be towards the left as given below, and towards the right on adding coagulating agents:

Death,	insanity,	normal,	insanity irritability,	sleep or anesthesia,	death.

Dispersion ⟵⟶ Coagulation

Let us see what can be made of these facts and postulates in a few specific examples.

Alcohol is credited with some 8 or 10% of the mental disorders that lead to hospital incarceration. Alcohol is variously described as: an intoxicant, stimulant, narcotic, antiseptic, disinfectant, hypnotic, astringent, etc. Actually it is only a coagulating agent, which defines all of the above terms as soon as the substrate upon which it acts is given. If we confine our attention to its action on the brain, it is agreed that alcohol first stimulates and then depresses, the depression passing into sleep, anesthesia, or death depending upon the amount taken. If taken repeatedly in appreciable amounts it will cause some interesting disturbances. The stimulation of the visual faculties will bring about "the snakes," while stimulation of the auditory regions will bring about hallucinations of hearing, and stimulation of other regions of the brain will bring about general mental confusion. The combination of these effects in various degrees will mark the person as temporarily insane. These effects are due to the initial decrease in dispersion of the colloids of the nervous system and are entirely physical in nature. Since the initial phases of coagulation are easily reversible, it is not surprising to find that these cases recover in a short time. There is another type of reaction obtained after excessive and long-continued use of alcohol, marked by a demented state of long duration with pronounced disturbances of the intelligence, memory, and judgment. It is frequently associated with actual damage to the nervous system (Korsakoff's Disease). This slow or incomplete recovery with damage to the nerves is clearly a case of coagulation that is difficultly reversible.

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[1] Bancroft and Richter: J. Phys. Chem., 35, 511 (1931).

The ability of alcohol to bring about alterations in the degree of dispersion of the colloids of the cell protoplasm is not hypothetical. Heilbrunn[1] has shown by means of his viscosity studies that this effect of alcohol is quite common. Marinesco,[2] using higher concentrations, was able to produce coagulations in the nerves of such density that he was able to photograph the colloidal change in the ultramicroscope. The mechanism of the coagulation with low concentrations of the material has been considered in another paper.[3]

Examples of damage to the nervous system, with the corresponding psychical changes, by means of known coagulating agents are very numerous. The action of lead on the nervous system is interesting. It is well known that lead salts can behave as coagulating agents towards bio-colloids. In fact their use in medicine as astringents and haemostatics depends upon this property. The effects of lead upon the brain are well known; it is found that there are but two phases of action.[4] In low concentrations or in the initial stage of poisoning, stimulation of the brain and of the optic nerves causes hallucinations of sight and mental disturbances which resemble those of delirium tremens. The second phase is exactly what one would expect of a coagulating agent. The stage of stimulation passes into depression, during which the early symptoms of paresis appear. In more advanced stages there is actual paralysis and damage to the nervous tissue. Lead is not alone in these effects; mercury, copper, and arsenic, which are coagulating agents, will cause disturbances of this type.[5]

Iodoform, an innocent coagulating agent, has a variety of actions that are understood best from a colloid point of view. The following quotation from "Useful Drugs" (1917) gives a good description of its effects. "Iodoform is a mild local analgesic, antiseptic, and stimulant. When adsorbed through the skin or from denuded surfaces, it produces intoxication which is not evident until after the lapse of some time. When swallowed, it is partially decomposed with the production of iodides which produce their ordinary effects. Part of the drug is adsorbed, however, in a form of combination not yet understood, and produces symptoms that are different from those ordinarily caused by iodine. Iodoform is excreted slowly, iodine compounds appearing in the urine for several days after a single dose.

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[1] "The Colloid Chemistry of Protoplasm" (1928).

[2] Kolloid-Z, 11, 209 (1912).

[3] Bancroft and Richter: J. Phys. Chem., 35, 215 (1931).

[4] J. F. Goodheart: J. Nervous and Mental Disease, 9. 435 (1882).

[5] Dana: "Textbook of Nervous Diseases" (1915).

"The symptoms are restlessness, anesthesia, sometimes unconsciousness, occasional convulsions, hallucinations, and delusions of persecution; rapid pulse and elevated temperature; in many cases collapse, coma, and death may follow." Here is a case where local anesthetic, stimulant, intoxicant, hypnotic, antiseptic, and disinfectant are combined in one and the same substance. This action can be best explained on a colloid basis as outlined in the first part of this paper. The stimulation both locally and mentally being associated with the initial destabilization of the tissue colloids, which is later followed by reversible coagulation producing the anesthetic effect, hypnosis, or antiseptic action. Disinfection and death are due to the irreversible coagulation.

Schede[1] discusses a number of cases of insanity due to iodoform. He describes cases where the use of iodoform has been attended with marked psychical symptoms. One type noted among children was a marked dullness of special senses. In adults he has seen great mental confusion produced by the external use of iodoform. In one case there was loss of personal identity, general mental confusion, loud singing, and violence.

The substances mentioned above are in no manner exceptional. There are a host of other coagulating agents that cause identically the same thing, to name but a few: morphine, henbane, cocaine, hashish, atropine, hyoscyamine, hyoscine, carbon bisulphide, tea, coffee, tobacco, and the interesting case of a mechanical blow upon the head. When one is struck upon the head, the preliminary stage of stimulation is passed through so rapidly that the effect seems only to be anesthesia or death. On recovery from such mechanical anesthesia the stage of stimulation can be seen as symptoms similar to those of intoxication. The case for the mechanical coagulation of the colloids of nerves has been discussed in another paper.[2]

Indirect narcotics, such as carbon monoxide, have been known to produce insanity. A more interesting type is that produced by lowering the pressure of oxygen in a medium that is breathed by the subject. The exclusion of oxygen will lead to an asphyxiation narcosis; but, if the oxygen pressure is not decreased that far, an interesting series of mental reactions is observed. Such cases are important, because it is recognized that aviators in flying to high altitudes become temporarily incompetent.[3] There is a height for each aviator above which it is not safe for him to go. This is termed his "flying ceiling." The symptoms of the disturbance produced by tensions of oxygen lower than this value are mental confusion, leading to errors of performance: sometimes hallucinations of sight and hearing were found; in some men an uncontrollable desire to sing and whistle were manifested.

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[1] Centr. Chirurgie, Nr. 3 (1882).

[2] Bancroft and Richter: J. Phys. Chem., 35, 215 (1931).

[3] Sheep: The Flight Surgeon, Air Service Information Circular. July, 1921; Bagby: Psychopathology under low Oxygen Tension, ibid. May, 1920.

In conclusion, we may sum up the effects of both the direct and indirect coagulating agents by pointing out that when they are acting upon a given substrate, the increasing instability of the colloids followed by a reversible coagulation, which may later become irreversible, is associated with the stimulation, depression or narcosis, and actual damage observed in that tissue. The stimulation in particular is important because it is believed to be the source from which some of the mental phenomena of insanity originate.

The important point is that not just any degree of dispersion of the cell colloids will satisfy the needs of the cell. There must be some normal and definite state of dispersion of the nerve colloids and any alteration from this normal state will bring about the same type of mental disturbance as is observed in cases with organic disorders. There are at least two major alterations that are possible; first a decrease in dispersion (coagulation) and second, an increase in dispersion (peptization). It has been shown that those coagulating agents that have a preferential adsorption for the higher nervous centers and bring about the alteration of the colloids of that tissue to a lower state of dispersion will reproduce phenomena that are associated with certain types of insanity.

The alteration of the cell colloids in the opposite direction, towards an increase of dispersion, are also of an interesting character. Such an alteration can be accomplished by the preferential adsorption of an ion that will increase the potential difference between the colloid and the surrounding medium, or by the adsorption of another colloid, and thirdly by the adsorption of water. These are the three methods commonly employed in the laboratory to bring about peptization. If something were known of the chemistry of nerve cytoplasm it would be possible to discuss clearly the possibilities of peptization. Dana[1] gives the necessary data. The reaction of the tissue is alkaline, water is the dispersing medium, the important thing being that "the albuminous substances, called also proteins by Halliburton, have little or no phosphorus and make up the most of the cell-body or the cytoplasm." Peptizing salts for protein material in an alkaline medium have already received the attention of chemistry; from the Hofmeister series it is known that bromides, iodides, and thiocyanates will show this property in an alkaline medium.

Deliberate studies of the physiological or psychological effects of peptizing agents on the nervous system do not exist. However, since the bromides, iodides, and thiocyanates have been extensively used without realizing that they were potent peptizing agents, the literature on these substances will furnish the necessary data if properly interpreted. Before considering the data it is well to point out that, since the increasing instability of the nerve colloids are associated with stimulation, stabilization would be expected to bring about the opposite effect, at least up to a certain point. Also, it must not be overlooked that while the bromides, iodides, and thiocyanates are peptizing agents in an alkaline medium, they are just as potent coagulating agents in acid medium. This point will be emphasized later.

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[1] "Textbook of Nervous Diseases" (1915).

Krosz[1] gives a good description of the effects of the bromides and a summary of the earlier literature. The bromides lower the reflex irritability, this is noticeable in the throat where the base of the tongue, palate, and pharynx are involved, making swallowing difficult and a perceptible slowing of speech. Mentally there is a feeling of exhaustion and confusion combined with a dimness of vision and a slight deafness. The heart action is slowed. Albertoni[2] showed directly that the bromides lowered the irritability of the brain. He exposed the brains of dogs and by means of electrical stimulation found areas that when stimulated would produce convulsions in the animals. The animals were then fed upon bromides and the experiment repeated; it was found that in consequence of the bromide ion there was an enormous reduction in this irritability. Similar results were obtained by Bickels and Zbyszewski.[3] Although bromides are frequently referred to as hypnotics, they differ in that bromides produce restfulness through lowering of the reflex irritability, thus permitting a normal uninterrupted sleep to be realized. It is for this reason that they are so effective in combination with a true hypnotic such as chloral.

Peptization, unlike coagulation, is not very rapid; hence the administration of small amounts over long periods of time shows some effects that are different from those of a single dose. When administered over long periods of time there is no great tendency to sleep and the motor regions lose their irritability to such an extent that paralysis results and continued administration at this stage produces death.

The effect of the iodides have been studied by M. Sgalitzer.[4] The decrease in respiration frequency, lowering of the temperature, slowing of the pulse, etc., are similar to that produced by the bromides. In high concentrations there is the decreased irritability of the motor regions which will pass into paralysis. It was noted that narcosis was not produced by the iodides. Death is due to the paralysis of the breathing center. The ready decomposition of the iodides in the body with the liberation of iodine and the additional effect of iodine upon the thyroid complicate the pure peptizing action somewhat.

The literature on the action of the thiocyanates upon the nervous system is not very extensive. As to be expected, their effects are not unlike those of the bromides and iodides in lowering the irritability of the motor regions.[5] The ability of the thiocyanates to cause mental disturbance has been noted. J. F. Borg[6] describes the condition: "Toxic psychoses developed in four patients, with disorientation, hallucinations of sight and hearing, mania, confusion, and ideas of persecution, singly or in combination. They lasted only from five to seven days after the drug was stopped. They were all in patients to whom it had been necessary to give large doses to obtain a desirable reduction [of blood pressure]." The thiocyanates have been the least studied of all the peptizing agents, although it is probable that they will show this property to a greater degree than any other ion.

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[1] Archiv. exp. Path. Pharmakol., **6**, 1 (1877).

[2] Archiv. exp. Path. Pharmakol., **15**, 251 (1882).

[3] Neurol. Zentr.. **17**, 1081; Zentr. Physiol., **34**, 366.

[4] Archiv. intern. Pharmacodynamie, **18**, 284.

[5] Münch. med. Wochenschr., **50**, 153 (1903); Centr. ges. Ther., **22**, 19 (1904); Med. Klinik, **8**, 234 (1912); Wiener klin. Wochenschr., **25**, 794 (1912).

[6] Minn. Med., **13**, 281 (1930).

Throughout this series of bromides, iodides, and thiocyanates two interesting side effects are always noticeable, namely, irritation of the stomach and the skin. It will be recalled that in acid media these ions are strong coagulating agents. Naturally the coagulating effect in the stomach is due to the acidity of the gastric juices and will lead to the nausea and vomiting that are frequently observed. The effect on the skin is also intelligible if it is remembered that in most cases the perspiration is acid in reaction,[1] naturally the effect of coagulation would be irritation.

The conclusions that can be drawn from the study of the influence of coagulating and peptizing agents on the nervous centers are evident. A variation in the degree of dispersion of the colloids of such tissue from the normal state will bring forth abnormal mental reactions that are found to be not unlike the phenomena of insanity. Hence it is not improbable that in mental disorders not directly traceable to any organic disturbances, the cause may be due to some variation from the normal state of the brain colloids. Such a point of view is of great service because it can explain the effects of drugs on cases of insanity, give a simple classification of the types of disorders, and at the same time suggest substances that would alter favorably the course of the disorder.

A few specific examples will clarify this position somewhat. If a case of mental disorder could be found that was due to the over-peptization of the brain colloids such a state would be favorably altered by coagulating agents, provided enough of the drug were given to decrease the dispersion to the normal state. Such cases that respond to treatment by coagulating agents are known and the following experiments make it seem highly probable that the abnormally high dispersion of the brain colloids are responsible for the condition. In 1916 Loevenhart, Lorenz, Martin, and Malone[2] were conducting experiments on stimulating the respiratory center with sodium cyanide. A very interesting observation was made in the case of a patient with dementia praecox. This patient had been mute for several months, but following the injection of sodium cyanide there was a short period in which "the patient made a few coherent and relevant responses to simple questions." This peculiar property of sodium cyanide is not very marked and the substance is unsatisfactory. Latèr carbon dioxide was employed as a stimulant with very striking results.[3] The results of this significant piece of work are best given in the authors' own words: "The most favorable and striking reactions occurred in those patients who had been mute and mentally inaccessible for long period of time. In these cases, after a short period of respiratory stimulation, this inaccessibility disappeared and the catatonia passed off. A number of patients have carried on conversation. A few mentioned depressive thoughts. One patient was markedly facetious, making responses typical of talkative hebephrenic dementia praecox. Another patient, the least reactive of those so far observed, showed only a disappearance of muscular tension and a voluntary looking about the room and at those standing near.

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[1] Hammarsten: "Text Book of Physiological Chemistry."

[2] Archiv. Int. Med., 21, 109 (1918).

[3] Loevenhart, Lorenz, and Waters: J. Am. Med. Assoc., 92, 880 (1929).

"A number of patients appeared frightened when the cerebral stimulation developed; they looked about apprehensively but became calm and at ease quite promptly when efforts were made to reassure them. In other words, they seemed to comprehend the situation correctly, and, following this almost immediately, they made coherent and relevant replies to questions. In one patient who had been mute for more than six years, the efforts at speech for about two minutes resulted in a jumble of unintelligible but speech-like sounds, after which the words became distinct and a successful conversation was held.

"The cerebral stimulation, as evidenced by free muscular movements, animated features, and ability to carry on conversation and to comply with requests has lasted from two to twenty-five minutes."

"During the period of cerebral stimulation, the inhalation of carbon dioxide and oxygen was stopped. If no more gaseous mixture is given, the patient gradually returns to his former condition. This return is as striking as is the development of increased psychic activity. Gradually the patient's attention can no longer be held; he ceases to respond to questions; muscular tensions redevelop, if previously present, and quite like the drawing of a curtain on psychic function, the patient returns to his former stuporous condition. In some cases, during the period of stimulated mental function, the patient responded quite like a talkative psychotic person, expressing many bizarre delusions and resembling in every way rather typical psychotic patients. In one notable case there was a prolonged period of from two to twelve minutes during which the patient maintained a comprehensive conversation without any evidence of psychosis; then quite suddenly the patient seemed to become frightened and began to express many delusions in a loud voice."

Since this manuscript was sent to the printer, there has appeared in the *New York Times* of March 29, an account of experiments by Dr. Karl Langenstrass on catatonic stupor at St. Elizabeth's Hospital in Washington. "Several years ago it had been observed that, by making the patient inhale a mixture of carbon dioxide and oxygen, it was possible to bring him back to consciousness for a period no longer than thirty minutes, during which he would behave in a normal manner. With this as a clue experiments were begun at St. Elizabeth's Hospital two years ago under the direction of Dr. Karl Langenstrass, who today described the results [at the annual clinical session of the American College of Physicians].

"Various ways of prolonging the period of recovery have been tried out. Beginning with a mixture of five percent carbon dioxide and ninety-five percent oxygen, the proportions were shifted gradually until it was found that a mixture of twenty-five percent carbon dioxide and the rest oxygen was the most advantageous. In addition to the inhalation treatment, Dr. Langenstrass told further that suggestion therapy, a mild form of hypnosis, was tried on the patient as soon as the gas mask was removed from his face after about half an hour of inhaling the mixture. Typhoid vaccine and coli fluid were also administered for the purpose of producing a rise in temperature.

"The net result, Dr. Langenstrass stated, is that one patient who had been in a mental stupor for over ten years has now been perfectly normal for the last two years. One woman is now supporting a drunken husband and three or four children. In all, three cases have been sent out into the world again functioning normally without any need of further treatment. The original treatment lasted for about a month."

Both sodium cyanide and carbon dioxide are known to be narcotic or coagulating agents, the carbon dioxide acting directly[1] while the sodium cyanide is an indirect narcotic.[2] It is to be noted that the reactions were observed before narcosis, or reversible coagulation was reached. It was also found that it was possible to narcotize a patient and observe the interesting phenomena after narcosis. W. F. Lorenz[3] describes the observations: "It was found that cases of catatonic stupor responded to this narcotic [sodium amytal] quite like a normal individual. That is, within 4 or 5 minutes, and before a total of 10 to 14 c.c. of the solution are injected they sink into deep sleep. The muscular rigidity disappears; the reflexes are abolished; breathing becomes slow and quite shallow; the systolic blood pressure falls 30 to 40 millimeters of mercury. After an hour the blood pressure returns to its former level; the patient can then be aroused and will respond to painful stimuli. Then follows a period of what appears to be normal sleep, the duration of which is largely determined by noises or other disturbing environmental influences.

"In the stuporous, catatonic cases we have seen prolonged periods of mental clearness following the state of deep narcosis. A brief account of one such case will serve to illustrate the striking change in mental condition, which is being presented. Case—T.W. (female); age 27; married and the mother of two children. She had been in a state of catatonic stupor for a period of four months when she was admitted to our service and sodium amytal administered. At this time the patient showed rather extreme muscular rigidity; active negativism; her limbs, head and body in a flexed position resembling the fetal posture. She had been tube-fed for over four months and voided involuntarily. Furthermore, she was in a state of extreme emaciation, weighing 66 pounds.

"This patient was given 1/2 gm. of sodium amytal dissolved in 10 c.c. of distilled water by intravenous route. Within 5 minutes she was in a state of deep narcosis. The muscular rigidity had disappeared; all reflexes, including the corneal, were absent. She continued in this state of deep narcosis for about an hour and then continued at a level of unconsciousness which could be influenced by slight painful stimuli. She remained in this condition another three hours, or a total of 7 hours, after the time of the injection. She was then aroused by speech and she responded to conversation, asked for food and drink. She continued in this aroused mental state for a period of four hours, when no further efforts were made to keep her awake and she dropped into what appeared to be a natural sleep for a period of five hours, when the mutism, muscular rigidity, and active negativism slowly redeveloped."

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[1] Heilbrunn: "The Colloid Chemistry of Protoplasm" (1928).

[2] Bancroft and Richter: J. Phys. Chem., **35**, 215 (1931).

[3] Psychiatric Quarterly, **4**, 95 (1930).

Looney[1] studied the blood analysis of catatonic patients and found that there was an abnormally low amount of calcium present and an increase in creatine. He raised the calcium content slightly, but there was no change noted in the clinical condition of the patients. His investigation is being continued in the hope "that it will be possible to raise the calcium values up to about 15 mg. and keep it there for a period of at least a week so that definite conclusions may be drawn as to whether such a change results in any diminution of the muscle tension."

English[2] has employed an interesting coagulating agent, manganese chloride, in the treatment of nervous disorders. The following case is quoted from his study as indicative of the effects of treatment: "W.G.H.—18 years; single. Catatonic schizophrenia. Nutritive condition poor and inferior muscular development. Was defective as a student. Symptoms exhibited three weeks previous to admission. Dull, stupid state changing to one of impulsiveness and he became sleepless, stubborn and negativistic. He lay in bed markedly indifferent and refused food, and, if up, would stand for a considerable time even if placed in an uncomfortable position.

"He was given a course of manganese chloride and his weight, which was 88 pounds before treatment, increased to 146 pounds. There was also a marked change in his mental condition—he is now bright in manner, tidy in habits and thoroughly mischievous and over active." The original work should be consulted for other interesting cases.

Berger[3] has also had an interesting experience with the effect of coagulating drugs and catatonic stupor. He injected eleven patients with small amounts of cocaine hydrochloride and noted that the majority became suddenly active after the first injection. Like some of the above cases, the improvement did not last more than an hour or two. His observations lead him to regard the basis of catatonic stupor as a diminution of the processes of dissimilation and of the cortical functions generally. He does not regard the theory of psychic origin of catatonic stupor with favor.

Such striking responses as the above cases to known colloidal coagulating agents cannot help but impress one that the stuporous catatonic state is associated with an over-peptization of the colloids; and that the gradual decrease in dispersion produced by the narcotics must pass through the normal degree of dispersion before the other extreme of reversible coagulation is reached. Conversely, if the brain colloids of such cases are coagulated reversibly and then allowed to pass slowly to the state of abnormally high dispersion, the system would again have to pass through the intermediate normal colloidal and mental state, as was found in the case that became normal anesthesia. The truth of this view is justified and strengthened in the fact that cases of mental disorders due to the opposite effect, i.e. decreased dispersion, can be materially relieved by peptizing agents. This statement will be made more convincing by illustration of facts.

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[1] Am. J. Psychiatry, 5, 213 (1925).

[2] Am. J. Psychiatry, 9, 569 (1929).

[3] Münch. med. Wochenschr., No. 15 (1921).

Substances that so decrease the dispersion of the colloids of the central nervous system that it is in a state of stimulation can be antagonized by peptizing agents. Januschke[1] investigated a number of such cases. He was able to produce epileptoid convulsions in guinea pigs by means of camphor; running movements and clonic twitching of the muscles were marked. This condition would be maintained for several hours and in most cases would end with the death of the animal. Large doses of bromides would suppress these effects and even small doses would cause a marked diminution in intensity. Also the clonic contractions of the muscles of rabbits produced by cocaine, which are caused by the stimulation of the higher centers of the cerebrum, can be antagonized by bromides. The effects of picrotoxin can also be diminished by the bromides. He also found that the tonic reflex convulsions produced by strychnine could be abolished by means of the bromides. Since the bromides had no influence on physostigmine, which does not affect the cerebrum, he concluded that the primary effect of the bromide ion was on this and other centers of the spinal cord.

The effects of bromides on epilepsy afford a very interesting study. The actual cause, or causes, of epilepsy are not known, so it is a functional disorder; some of the external symptoms are produced by a host of toxic agents such as alcohol, lead, camphor, etc., and even by mechanical injury to the head. It does not seem improbable that in some cases a decrease in dispersion of the colloids is associated with the disorder. Dana[2] in speaking of the pathology says: "It is probable that in true epilepsy there is an instability of certain cell layers of the cortex cerebri and a tendency to degenerate". Degeneration from a colloidal viewpoint is nothing more than the coagulation and subsequent digestion of the involved structures, as it is impossible to digest peptized substrates. As already indicated, the phenomena of epilepsy are similar to those produced by stimulants, so it is no surprise to find that in many cases the phenomena can be antagonized by peptizing agents such as the bromides.

An unbiased account of the effects of bromides on epilepsy can be found in "Modern Medicine" by Osler and McCrae. They point out that "in view of the fact that the number of individual attacks is usually so speedily reduced by the exhibition of bromides, even to the entire suppression of them, the hope that the drug is a real curative agent in the disease has been and still is widely held. So great has been the reliance upon the bromides that real scientific therapy has actually been delayed by this erroneous empiricism.

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[1] Z. ges. exp. Med., 8, 17; Med. Klinik, 10, 389 (1913).

[2] Text Book of Nervous Diseases" (1915).

Until a few years ago the almost wholesale use of the drug made it possible for a public clinic to count the cases showing bromide poisoning as the rule rather than the exception. Happily the recognition that there is an acquired art in the use of bromides is removing this reproach.

"The whole plan of treatment including the bromides should be continued for years even though the attacks should cease. Some authorities regard the plan of successful routine a necessary plan of life henceforth; its long continuance after attacks have ceased (for several years at least) seems to upbuild and make for permanency of the restored normal psyche."

Wright[1] has recently studied the use of the bromides in functional disorders. He noted that the conditions which best respond to the bromide treatment were cases in which there was some degree of tension. Most of the cases in which the bromide treatment failed were found to occur in states of apathy.

If the disorders in epilepsy are due to an instability of the colloids with a tendency to decrease in dispersion, there should be two methods of relieving the symptoms. The first of which has already been discussed, i.e. peptizing effect of the bromides. It has already been indicated in the first part of this paper that a coagulating agent affects a normal tissue by first stimulating, then depressing the tissue. The depression passes slowly into sleep, narcosis, or death, depending upon the concentration of the drug and reversibility of the coagulation. If the tissue is in the stage of stimulation, as in epilepsy, then small amounts of narcotics will relieve the hypertension, because it will merely push it into the initial phases of the depression preceding narcosis. It is to this fact that the barbituric acid derivatives owe their popularity in the treatment of epilepsy.

The bromides have other interesting properties that would justify a more intensive investigation. In a recent paper we pointed out from theoretical reasons that peptizing agents might have a favorable effect in the treatment of drug addicts.[2] Since then our attention has been drawn to several interesting cases of this type.

MacLeod,[3] in 1897, treated a patient, suffering from migraine and a highly nervous state, with bromides. The patient was also a confirmed morphine addict. The course of the treatment was such that the patient was in a deep stupor for several days such as that produced by the bromides. Upon recovery from the effects of the bromide he noted: "To her own astonishment and that of the sisters (she had been in their charge previously) she had no desire for morphine from the time she entered the hospital, and I am glad to say it has not yet returned.

"This case was, so to speak, cured by mistake and is all the more interesting that the patient had no desire to be cured, as she had informed me on several occasions. Naturally desirous of being certain how far the bromidism contributed to the result, I determined to test the question by excluding other conditions."

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[1] Am. J. Psychiatry, 5, 365 (1926).

[2] Bancroft and Richter: Proc. Nat. Acad. Sci., 16, 573 (1930).

[3] Brit. Med. J., 1897, 76.

His next case was that of a pilot on a boat who was a confirmed morphine habitué. The patient underwent a heroic treatment with the bromides and upon recovery was rejoiced over his deliverance from the craving for the morphine. An interesting side-light of this case was that he also lost the desire for liquor.

These are not isolated cases; the treatment was tried on several other drug habitués with favorable results in all except one case, which succumbed due to an error of the nurse in giving an overdose of the bromide.[1] Among these MacLeod says: "It is noteworthy that the loss of alcoholic craving in the second case was pointed out by the astonished patient himself."

Naturally, such interesting observations did not wait long before they were confirmed by other workers. Church[2] in America discussed the dangers of the treatment and apparently the whole matter was dropped. The unfavorable results were never due to lack of care, but more to the excessive doses of bromides. It should not be forgotten that it has never been shown that such large doses of bromides are necessary. As already mentioned, peptization is not rapid; hence the giving of bromides until toxic symptoms appear is dangerous, because the full toxic effect is somewhat delayed. The bromides should never be given to a patient with acidosis.

We do not wish to give the impression that drug addiction and its cure is all a purely colloidal problem. It is very important in treating addicts to hasten the elimination of the drugs from their system. In fact all the present-day treatments employ this as a preliminary measure; the next important thing is to restore the nerve colloids to their normal state, and this is best done only by colloidal means, such as peptization. The purging, education, hospital care, etc., of the patient are just as important but are not colloidal in nature and so have found no treatment in this paper.

Quite aside from this, the mere fact that a plausible explanation has been given to the action of the bromides, it would seem that medical interest would be centered in other peptizing drugs. Both the iodides and thiocyanates have this property to a greater degree than the bromides. The iodides cannot be employed very well due to their unfavorable effect on the thyroid. However, the thiocyanates offer many interesting possibilities both in the treatment of epilepsy and drug addiction that would justify a very careful and comprehensive study.

The bromides do not stand alone as examples of peptizing agents employed in medicine. The iodides have a limited application in the treatment of certain metallic poisonings, notably lead, mercury, and arsenic. As has already been indicated, the mental disturbances brought about by some poisons are similar to those shown in insanity. Clevenger[3] observed a case of lead poisoning in which the symptoms of mute depression, observable in ordinary melancholia and epileptiform convulsions were present. He treated the patient with potassium iodide and in a short time the patient was discharged as fully recovered. He points out that "had the cause of this attack been unascertained, the patient would have died insane." Osler[1] gives a short summary of the use of the iodides in the treatment of cases of lead, arsenic and mercury poisoning.

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[1] MacLeod: Brit. Med. J., April 15 (1899).

[2] N. Y. Med. J., **71**, 904 (1900).

[3] Nervous and Mental Disease, **11**, 308 (1884).

Naturally the manner in which the iodides relieve the symptoms of such cases is an interesting topic. On first thought it might seem that the iodides form insoluble iodides with the metals and thus antagonize their action. This cannot be the complete story however, for the iodide of lead, for example, is soluble to the extent of 0.0442 gms. per 100 c.c. while lead chromate is soluble to the extent of 0.000007 gms. per 100 c.c. Yet lead chromate can easily bring about lead poisoning. While the amount of lead required to bring about poisoning is not known with great exactness, Brouardel considers that 1 mg. daily is sufficient. The treatment requires 0.3 gm of potassium iodide three times daily so that it seems quite necessary that an excess of iodide be present. This excess iodide undoubtedly behaves in the body as it does in the laboratory and merely serves as a powerful peptizing agent to the coagulated colloids of the nervous tissue.

This is by no means an exhaustive treatment of the subject dealing with the effects of colloidal reagents on the nervous system; the examples may be multiplied many fold, but the basic causes always come back to the alteration from the normal state of dispersion of the cell colloids. All of the work has been carried out by medical research workers who do not take into consideration that the materials they are dealing with are the best-known colloidal systems and that the drugs they use are potent reagents that will bring about colloidal changes in the tissues. Such a state of affairs is not conducive to a rapid advancement in knowledge concerning functional disorders. It is the hope of the authors that this paper may, in a small way, stimulate such workers to recognize that there is no sharp boundary between medicine and colloid chemistry, and that their researches are incomplete if they have not either included or excluded the variations of the tissue colloids in the pathological conditions.

Summary

(1) Medicine regards the major mental disorders as organic or functional disturbances. The causes and ideas of functional abnormalities are very hazy and incomplete.

(2) It is shown that while modern histological methods are well adapted to show the usual type of organic troubles they are absolutely inadequate to demonstrate the most characteristic property of living matter, i.e. the colloidal state, and its variations.

(3) The suggestion is made that many of the "functional disorders" may be nothing more than an abnormal degree of dispersion of the nerve col-

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[1] "Modern Medicine" (1915).

loids and have erroneously been classified as functional due to the inability of the histological technique to reveal the colloidal abnormalities.

(4) A study of the effects of known coagulating agents on the normal nervous system reveals that such colloidal reagents will produce symptoms that are not unlike many of those of insanity.

(5) The effects of peptizing agents are similar in many respects to other disorders.

(6) This is definite proof of the view that there is a normal state of dispersion of the nerve colloids and that any alteration from this state will bring about abnormal mental reactions.

(7) It is suggested that disorders of over-dispersion may be benefited by coagulating agents, and disorders of decreased dispersion would be improved by peptizing agents.

(8) Some physiological symptoms of catatonia are similar to the effects produced by peptizing agents. The striking results obtained in treating catatonic patients with coagulating agents indicates that this disorder may be due to the over-peptization of the colloids.

(9) Some of the symptoms of epilepsy can be reproduced by known chemical and physical coagulating agents. Both the symptoms produced by these agents and that of epilepsy are antagonized by peptizing agents such as sodium bromide.

(10) Other disorders, due to the use of coagulating agents, such as are found in drug addiction can be relieved by means of peptizing agents.

(11) The beneficial effects of potassium iodide in lead, arsenic, and mercury poisoning is another example of disorders of decreased dispersion being improved by peptizing agents.

(12) Coagulating agents cause changes in the brain colloids from normal through irritability and insanity to sleep or anesthesia, and death. Dispersing agents cause changes in the brain colloids from normal through insanity to death.

Our thanks are given to Dr. Seymour DeWitt Ludlum[1] of Philadelphia, who is primarily responsible for our starting on this investigation.

Cornell University.

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[1] S. DeW. Ludlum and A. E. Taft: Trans. Am. Neurological Ass., 1927); Alexander's "Colloid Chemistry," **2**, 695 (1928).

ROTATION AND CONFIGURATION IN THE WALDEN INVERSION*

BY WILDER D. BANCROFT AND HERBERT L. DAVIS

In the past thirty years one of the important fields of research in organic chemistry has been the investigation of the phenomena commonly grouped under the heading of the Walden inversion. In general this work is an attempt to ascertain the course of more or less common reactions in organic chemistry with the special purpose of discovering if and when one group directly takes the place of another group or when the entering group occupies some other position in the molecule than that originally occupied by the displaced group. The latter is what Fischer called the Walden Inversion because it was first observed by Walden in 1895.

Study of these phenomena and of the literature dealing with them leads one inevitably to the conclusion that the crux of the whole matter is that no one is yet able definitely to correlate the configuration of any two related compounds as this configuration is revealed by their optical rotation. As long as there is a lack of such knowledge it will be impossible to tell *when* a Walden inversion takes place, to say nothing about studying the conditions which tell *why* or *how* such an inversion proceeds. That this problem is of great importance is testified to by Stewart[1] who says: "In the whole field of stereochemistry, no more puzzling phenomena are known than those grouped under the head of the Walden Inversion, and at the present time we still await a solution of the problem. The data are so complicated that it would be impossible to deal with them fully here."

The present paper proposes a return to, and more rigid adherence to, the criteria laid down by van't Hoff to govern the observation of the rotatory power of a substance. It offers also a method of correlating optical active substances with one another and with their rotatory power, and finally applies these criteria to some of the more common substances and reagents employed in the Walden inversion, classifying them into substances and reagents whose reactions are or are not characterized by Walden inversions.

Much of the work on the Walden inversion has been done with the hydroxy acids, and the examples selected will be of that type, although nearly all types of optically active compounds have been at one time or another the object of this sort of investigation. Early in the discussion it should be emphasized that there is no immediate connection between the sign of rotation and the configurations of two related compounds. Thus, merely because the chlorosuccinic acid derived from l-malic acid possesses the opposite rotatory power, one is not justified in assuming that an inversion took place during the reaction. The inversion is solely a matter of changed configuration and

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[1] Stewart. "Recent Advances in Organic Chemistry," 2, 16 (1927).

as yet we do not know that in this case a changed configuration is associated with a change in sign. It will be shown later that this is probably so in the malic acid series, but generalization is not simple. This all leads to an immense amount of confusion and the custom has grown up, following Fischer's sugar work, of designating compounds not merely "*l*" or "*d*" but we find various compounds called "*l*(+)", "*l*(−)", "*d*(+)", *or* "*d*(−)". This means that a given compound may belong to the "*l*" series so far as configuration is concerned and possess either dextro or levorotation. In the designation of the series to be used, most authors agree in selecting natural *l*-malic acid as the typical example of the "*l*" series configuration while natural tartaric acid is the type compound of the "*d*" series, and most determinations of configuration go back to these compounds or their derivatives as the starting point. The great difficulty of this method of representation is that the conclusions reached by any single investigator are not those of any other, and consequently the letter designating a given compound may vary from author to author while the sign of the rotation will usually be the same, if observations were made under similar conditions. This all appears, and is, very perplexing, but no remedy for the situation is in sight unless we can agree on some criteria to correlate the configurations as is attempted here.

In order to make the problem as concrete as possible a typical case involving the Walden inversion, and the first one discovered, will be outlined. It is from the malic acid series.

$$\text{(I) } l\text{-malic acid} \xrightarrow{PCl_5} \text{d-chlorosuccinic acid} \xrightarrow[\text{aq. solution}]{\text{in acid}} \text{d-malic acid}$$

$$\text{(II) } l\text{-malic acid} \xrightarrow{PCl_5} \text{d-chlorosuccinic acid} \xrightarrow[\text{aq. solution}]{\text{in alkaline}} l\text{-malic acid}$$

Case (I) represents the simplest case of a Walden inversion for there can be little doubt that the two oppositely rotatory malic acids possess opposite configurations, or are antipodes. The doubt in this case comes when one attempts to answer the question, "In which of the two reactions did the inversion occur?". Case (II) will be explained if there is either no inversion in either reaction, or there is inversion in each of the reactions; in case (I) there can be inversion in only one of the two reactions. There are two possible solutions to the problem; the one is that the action of the PCl_5 is normal and without inversion and that the d-chlorosuccinic acid is of the same configuration as the l-malic acid and that consequently the hydrolysis in acid solution is accompanied by inversion while that in alkaline solution is normal and without inversion. The other solution, and the one which in view of other evidence seems more probable, is that the replacement of hydroxyl by chlorine is here accompanied by inversion and that the acid hydrolysis is normal while the alkaline hydrolysis is abnormal. It is now seen that the final solution of this typical problem of the Walden inversion will not be reached until we are able to say definitely that d-chlorosuccinic acid is of the same configuration as *l*-malic acid, or is of the opposite configuration. Since there will be always at least two reactions between an optically active substance and its antipode, as in this case, this question will arise in every investigation of the Walden inversion. The fundamental importance of the correlation between optical rotation and the configuration of these compounds is obvious.

There have been several criteria proposed to establish this correlation and a few of them will be briefly reviewed. For many years Freudenberg has studied this problem, principally by means of reactions in which the groups directly attached to the asymmetric carbon atom were not replaced as a whole but were altered in steps. In one of his later papers[1] he expresses his conclusions to the effect that natural (+) lactic (sarcolactic), (−) halopropionic acids, (+) alanine, (−) malic, (−) monohalosuccinic acids, and (+) asparaginic acid all belong to the l-series. If this conclusion that l-malic acid is of the same configuration as l-chlorosuccinic is accepted, then it follows that the reaction involving phosphorus pentachloride proceeds with inversion, that is, the chlorine goes in at a different position in the molecule from that just vacated by the hydroxyl group. Correspondingly, hydrolysis in acid solution proceeds normally while inversion attends the hydrolysis in alkaline solution. This is in accord with the conclusions reached by applying the criteria of this paper, as indeed are the rest of Freudenberg's classifications.

Another method of configuration determination was proposed by Hudson in relation to the amides. This rule proposed that those hydroxy acids whose amides are dextrorotatory be designated "*d*" acids. Freudenberg amended this rule to read that all such acids are to be designated as d-acids of which the amides have a higher dextrorotation than the free acids. This amendment was made to permit the inclusion of l-mandelic acid in this series.

Some d-acids.

d-Lactic	−2.5° to −4°	d-Lactamide	+ 22°
d-Glyceric	−2.1°	d-Glyceramide	+ 66°
d-Malic	+3° to −3°		
d-Malamidic	+9.3°	d-Malamide	+ 40°
d-Tartaric	+6 to +14°		
d-Tartramidic	+64°	d-Tartramide	+106°
levo-Mandelic	−153°	levo-Mandelamide	−95.5°
Hexahydro-levo-Mandelic	−26.6°	Hexahydro-levo-Mandelamide	+41.7°

Freudenberg[2] made the inclusion of the mandelic acid after the preparation of the last-named acid and its amide, arguing that the hydrogenation of the mandelic acid would have no effect on the configuration and that since the hydrogenated acid was of the d-series according to the rule of Hudson, so also was the original mandelic acid. Thus the replacement of the carboxyl hydroxyl group by the amino group produced a change in rotation ranging from 6° to 68° in the dextrorotatory direction. Similar substitution in l-malic acid produces a comparable increase in levorotation. It will be shown more at length later in this paper that the lactic acid which is here classified as d-lactic acid gives the levorotations here listed in aqueous solution but gives dextrorotatory salts and esters which show the acid to be truly of the d-configuration. In the same way d-malic acid in concentrated solutions gives the levorotation here mentioned, while in dilute solutions the dextrorotation becomes evident. The inclusion of the mandelic acid will also be justified later.

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[1] Freudenberg and Lux: Ber., **61B**, 1083 (1928).

[2] Freudenberg, Brauns, and Siegel: Ber., **56**, 193 (1923).

One of the first attempts at correlation of the forms of optically active substances was made by Fischer, who concluded that dextro-tartaric, dextro-malic, and levo-aspartic acids were configurationally related. More recently Freudenberg and Braun have converted d-tartaric into d-malic acid and l-malic into d-glyceric and further into dextrolactic acid (should be l-lactic). As a result of these experiments it appears that d-tartaric, d-malic, l-glyceric, and l-lactic (the two last should be d-) all belong to what is called the "*d*" series. Hudson and Levene have extended the work of Fischer to the sugar acids and simpler aliphatic acids, using the amide rule as one method of attack.

Some very extensive investigations of this problem have been based by Clough on the assumption that substances of similar configuration would exhibit similar changes in specific rotation under the influence of the same external conditions such as temperature, solvent, the presence of foreign substances such as inorganic halides, and certain substituents either on the asymmetric carbon atom or in another group such as the carboxyl group in the molecule. In this work Clough[1] agreed with the previous workers in regard to the four acids just named and added to that list some other hydroxy acids. His classification is made because the acids, their salts and esters and some derivatives behave similarly, in that rise in temperature makes them more strongly dextrorotatory, dilution of the aqueous solution increases the rotation, the sodium and potassium salts are more dextrorotatory than the free acids, and inorganic halides affect them in the same way—making them more levorotatory. None of these tests can be applied too strictly and Clough himself says there are some important exceptions to the rules. For instance, the rule provides that the substance show a positive coefficient of rotation with rise in temperature and yet such important substances as methyl and ethyl tartrates show diminishing rotatory power with rise in temperature. These same esters in the presence of salts show increasing rotations as does free tartaric acid itself.

A review of the literature on these relationships and of his own important work on them has been made by Levene[2] who finds general agreement on the configuration of the hydroxy acids but comes to different conclusions regarding the chlorosuccinic acids. He agrees with Holmberg[3] in designating the levorotatory halosuccinic acids as of the d-configuration while Freudenberg calls them of the l-configuration. Holmberg concludes that so far there is no general method available for ascertaining the configuration of mirror image isomers. Those offered are objectively unsatisfactory and allow subjective evaluation of evidence leading to conflicting results.

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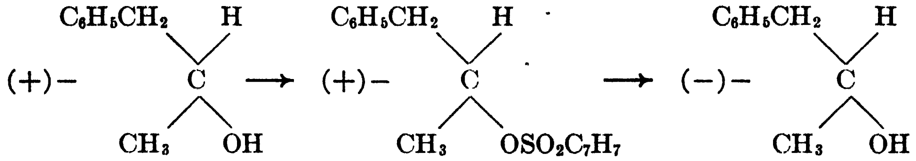
[1] J. Chem. Soc., **113**, 526 (1918).

[2] Levene: Chem. Rev., **2**, 179 (1925).

[3] Holmberg: Svensk. Kem. Tid., **41**, 60 (1929); Chem. Abs., **23**, 3441 (1929).

Before leaving these attempts to establish relative configurations, it might be well to point out that just as we know that many of the reactions involving the groups attached to the asymmetric carbon atom proceed with inversion and that therefore such reactions are of very doubtful value in determining whether an inversion took place or not, so also there is some evidence to the effect that even when the reaction does not affect the asymmetric carbon atom directly but only involves change on groups attached to a neighboring atom, still change of configuration may occur. Fischer[1] attempted to answer this question through successive reactions interchanging two groups on the asymmetric carbon atom and thus producing the optical antipode to the original substance. According to this the configuration of the asymmetric center remained unaffected by substitutions.

Quite otherwise, however, is the evidence in the esterification and subsequent hydrolysis[2] of the (+) benzyl-methylcarbinol which produced the oppositely rotatory product.



Wittig, in his discussion of this case, says that this reaction, although the formula recognizes no substitution on the asymmetric carbon, may nevertheless be brought into the series of the Walden inversion if one assumes that the mechanism of the reaction is such as to separate the ester group directly from the asymmetric carbon:

$$>\!\!-C\ \left|\underline{OSO_2C_7H_7 + H}\right|\ OH$$

and not from the oxygen atom:

$$>\!\!-CO\ \left|\underline{SO_2C_7H_7 + HO}\right|\ H$$

A summary of several such cases has been made by Kuhn[3] which indicates that, while such reactions are not common, they are by no means impossible.

After thirty years of the most extensive investigations of the Walden inversion it seems a pity that we are no nearer being able to tell when an inversion takes place. We know they do take place; indeed Werner claimed that the inversion was the ordinary method for reaction to proceed and that direct replacement was the exception. That does not appear to be well founded and most of us still look upon the inversion as an abnormal course for a reaction to follow—possibly because up to the time of Walden's observations that was the only possibility that had been thought of. Most of us still continue to try to divide these reactions into the normal and the inversion reactions.

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[1] Fischer: Ber., 47, 3181 (1914).

[2] Phillips and Kenyon: J. Chem. Soc., 127, 399 (1925); cf. Hückel: Z. angew. Chem., 39, 842 (1926).

[3] Kuhn: Ber., 58, 2088 (1925).

This attempt meets with several specific difficulties. It is not always easy to decide just what the rotation of a given compound is. Natural malic acid is dextrorotatory in the fused state or in concentrated aqueous solution; its dilute solutions, salts and esters are levorotatory. It is called l-malic acid. The opposite is true of natural tartaric acid and it is called d-tartaric acid, these two being taken as prototypes of configuration. This difficulty of having the rotation of an acid in concentrated or even in moderately dilute solutions in the opposite sense to that of its salts and esters is a common one. It is even more troublesome in the case of the amino acids. The amino acids of the succinic and propionic series are weakly rotatory and their rotation and solubility are both enhanced in acid solution where, of course, salts may form. Therefore they are usually examined in acid solution. Natural aspartic acid is dextrorotatory in aqueous solution or in acid solution but in alkaline solution it is levorotatory and its esters are levorotatory. The same things are true of alanine, or alpha amino propionic acid. With all this uncertainty these same amino acids are most common and often used in the Walden inversion. Many of these substances show widely varying rotatory powers depending on the state in which they are observed, as liquid esters, etc., or in varying concentration in varying solvents. One of the first necessities should be to establish some common state in which these substances may show their true activity in order that we may arrive at some logical conclusion concerning their configuration. This was done years ago by van't Hoff [1] and some quotations from him should make clear the necessity of adopting such standards. Chapter VII of this treatise is entitled, "Numerical Value of the Rotatory Power," and some quotations will be selected from this chapter.

Factors recognized as affecting the rotation include the wave-length of light, the solvent, and the temperature. Then, p. 134;

"It is certainly inadmissible to use simply the figures obtained by an examination of the substance without special precautions, because the size of the molecule is then uncertain, and the magnitude of the rotation seems to be specially influenced by every change in constitution. In this connection it is important to remember the fact recently discovered by Ramsay, that, of fifty-seven liquids examined, no less than twenty-one possessed double molecules, among them the alcohols, acids, nitro-ethane, acetonitrile, and acetone. Another objection is that the rotation is generally influenced by the solvent, and, indeed, by every solvent differently, perhaps in consequence of the four groups attached to carbon being differently attracted. If the substance be used alone, without solvent, its own molecules may be supposed to exert a similar influence, an influence displayed most prominently in the formation of crystals, and which, in the case of strychnine sulphate, e.g., leads to the almost complete annihilation of the rotation.

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[1] van't Hoff: "The Arrangement of Atoms in Space," (1899).

"The objections mentioned disappear completely only when the substance is examined in the state of rarefied gas. As this is impracticable, we are driven to adopt some other means, and thus arrive naturally at the state of dilute solution. It is also indispensable, of course, to take into account the molecular weight, which can then easily be determined; while the comparability of the results will evidently be by far the greatest when the same solvent is chosen for the different cases.

"The influence of wave-length and of temperature seems not to be important if the circumstances of each case are duly taken into account. The anomalous rotation-dispersion in the case of, say, tartaric acid in aqueous solution—which is such that the rotation changes its direction with the color—is evidently connected with the phenomena of equilibrium which affect the tartaric acid in the solution; it was also found by Biot in a mixture of right and left-handed substance[s]. The same holds for the great alteration in the rotation of tartaric acid when the temperature, the concentration, or the solvent is changed. All these phenomena are connected together and only make necessary a careful use of the figures obtained, but are no argument against the existence of relations between rotation and constitution in general."

In the next section, van't Hoff shows the applicability of the law of Oudemans-Landolt, according to which the rotations of the various salts of an optically active acid or base extrapolate to the same value for the rotation of these salts in dilute solutions.

"In these investigations the theory of electrolytic dissociation is a valuable guide; it enables the Oudemans-Landolt law to be predicted, and sees in the equality of rotation of the different salts the consequence of the existence of the same ions."

From a table van't Hoff selected the following numbers as representing the specific rotation of the ions in question.

Tartrate	43°	Diff. 14
Acid tartrate	29°	
Malate	14°	
Acid malate	9°	
Glycerate	22°	
Methoxysuccinate	15°	Diff. 14
Acid methoxysuccinate	29°	
Ethoxysuccinate	23°	Diff. 14
Acid ethoxysuccinate	27°	

"From this we see at once that, when the rotation alters on dilution, only the values at the limit are to be taken, and doubtful cases may be decided by a determination of the conductivity—i.e. of the molecular weight—accompanying the observation of the polarization."

The next section deals with the "Rotation of Imperfect Electrolytes. Organic Acids" and we find, p. 141:

"These substances demand separate treatment because, representing as they do the transition stage between electrolytes and non-electrolytes, they exhibit—in aqueous solution at least— complicated phenomena, which, however have already been partially accounted for. In view of the alteration of the molecular conductivity and of the lowering of the freezing-point with the concentration of their solutions, it is evident that water effects a fundamental change in their molecular structure—dissociation, in fact. The salts, especially those of strong acids and bases, show this at degrees of dilution which admit of an optical examination, and then Oudemans' law holds. With the acids this is not the case."

Van't Hoff then gave data to show that while the non-electrolyte sugar and the electrolyte disodium tartrate show relatively slight changes in rotatory power as the solutions are diluted, the imperfect electrolytes tartaric and malic acids showed very large changes, in the case of malic acid a change from right to left being observed as the solution is diluted. He proceeded to deduce five laws governing these complex phenomena.

"1. The alteration in rotation effected by change of concentration is parallel with that effected by change of temperature, dilution and rise of temperature acting in the same direction, as in general both have the same effect on dissociation. For sugar and the tartrates the alteration with the temperature is scarcely perceptible. With tartaric acid, warming like dilution effects a rise. In the case of malic acid, Pasteur found in the dilute left-handed solution an increase of rotation to the left on warming, which is the result Schneider obtained by dilution. With mandelic acid Lewkowitsch observed a decrease in the rotation on diluting and on warming; with rhamnose Tollens found the same thing.

"2. The change of rotation with the concentration is parallel with that effected by the solvent, so that the rotations in other solvents approximate to those in concentrated aqueous solution. Tartaric acid, which in water gradually rotates less to the right as the concentration increases, exhibits in other solvents now a weak right-handed rotation, now even left-handed rotation as in alcohol.

"3. The change of rotation on dilution is in the direction of the numbers obtained for the [acid] salt, and appears to be limited by these numbers. It is again, in the case of tartaric acid that the subject has been most thoroughly investigated." Data show this to be true of tartaric acid and of malic acid. "Lactic acid, the right rotation of which is diminished by dilution (21.24 per cent. $(a)_D = 2.66$; 15.75 per cent. $(a)_D = 2.06$), possesses accordingly left rotation in its salts."

"4. The acids which undergo no change of rotation on dilution are also those which rotate as strongly as their acid salts. Methoxy- and ethoxy-succinic acids exhibit rotations which scarcely alter with the concentration and these rotations are almost the same as those obtained for the acid salts." The same situation prevails with quinic and shikimic acids.

"The hypothesis of electrolytic dissociation explains these facts to this extent, that it demands that dilution of an acid and salt formation shall bring about equal activity, since both cause the formation of the same ion. For dibasic acids the same holds for the acid salts, because dilution of these acids first liberates a single hydrogen atom.

"Evidently, however, there is something else concerned beside electrolytic dissociation, and that is the point of attack offered to the carboxyl group in another part of the molecule, as appears from the following.

"5. Great change of rotation on dilution manifests itself especially with the oxy-acids. Malic acid is remarkable in this respect. The change of rotation which we have observed to characterize this acid is no longer found in methoxysuccinic acid and in the corresponding ethyl derivative, nor in chlorosuccinic and acetylmalic acids. Thus when the hydroxyl group disappears, the rotation becomes more constant. The peculiar part played by this group is, however, still more plainly manifested in the gradual change which often occurs in oxy-acids after a change of concentration or of temperature. This was first observed in the case of lactic acid, the rotation of which decreased on simple standing of the freshly prepared solution; it was recently proved in the case of glyceric acid, and is due to etherification or lactone formation, as Wislicenus showed. This will be considered in the next section.

"In the oxy-acids, then, the alteration of the rotation on dilution may be due to a phenomenon akin to lactone formation, which also is probably influenced by electrolytic dissociation. Finally, several acids, and not oxy-acids only, possess a double molecule, and accordingly on changing the concentration they make break up in a way which will affect the optical examination. *Comparable results for acids are therefore scarcely to be obtained except by an investigation of dilute solutions of the alkali salts.*"

We shall at once make use of these criteria. In the case of malic acid (hydroxysuccinic) there is little doubt that the levorotation of the dilute solutions, of the salts, and of the esters fixes the true rotation of the malate ion as levorotatory. Aspartic (aminosuccinic) acid on the other hand offers more difficulties in that its rotation free in aqueous solution is dextro as is also the case for the acid solutions. But the levorotation of its salts and esters fixes this form of the natural aspartic acid as actually levorotatory. The statement of Holmberg that the natural dextrorotatory aspartic acid and the natural levorotatory malic acid are of the same configuration then takes on some meaning and when supported by other evidence to be offered later will be seen to be true. This is the aspartic acid which with nitrous acid gives l(-)malic acid and with nitrosylchloride gives l(-)chlorosuccinic acid.

The situation in the propionic acid system is similar. Natural or sarcolactic acid is dextrorotatory in aqueous solution, and its salts and esters give levorotations. This is the form which Walden properly wished to call l-lactic acid but there seems to be no real agreement to follow his suggestion even though it does represent the facts. The general form of the dilution-rotation curves for lactic and for malic acid is similar. The difference lies in the fact that in the lactic acid we are not able to follow the change into levorotation while with malic acid this is easy. The literature of alanine (aminopropionic acid) is less clear but it seems certain that the so-called d-alanine should actually be called l-alanine since it gives levorotatory esters and produces with nitrous acid a lactic acid whose zinc salt is levorotatory and with nitrosyl bromide a levorotatory α-bromopropionic acid.

The halogen-substituted acids of these two series present no problems for in as much as their rotations differ little with concentration, so also do the salts and esters present the same direction of rotation as the acids themselves.

Now that it has been established just what acids we are thinking about, we may take the next step and correlate the configurations in each series. The reactions just mentioned for the acids will not serve for this purpose since we do not know whether or not they involve the Walden Inversion or are examples of normal direct replacement. To correlate the configurations we shall return to the treatment of van't Hoff and employ a criterion which even in his day was known to have exceptions and weaknesses but which did serve in numerous cases. We offer this, therefore, as a first approximation and justify it empirically until a better criterion be found.

This citerion is that the rotation of an optically active molecule can be expressed in terms of some characteristics of the four different groups attached to it. The theories of Guye and of Crum Brown were expressed by van't Hoff in the equation;

$$P = (g_1\text{-}g_2)\ (g_1\text{-}g_3)\ (g_1\text{-}g_4)\ (g_2\text{-}g_3)\ (g_2\text{-}g_4)\ (g_3\text{-}g_4),$$

where P is the product of asymetry, determining the rotation, and g_1-g_4 are the group-weights in question, p. 155.

"This expression is not a necessary consequence of Guye's conception, but only a formulation of it upon certain assumptions made for the sake of simplicity. It is to be regarded as a special case of the view of Crum Brown, according to which K and g are identical. Finally, we may repeat that the essential requisite, that $P = 0$ when two groups are identical, is fulfilled; and that if two groups, g_3 and g_4, e.g., change places, the sign of P is simply reversed, its numerical value remaining the same.

"From this view the following novel and essential consequences result. If the groups are in the following order:

$$g_4 > g_3 > g_2 > g_1,$$

and the substance is, say, right-handed, then when g_4 is replaced by smaller and smaller groups, we may expect:

1. Diminution of the right rotation for $g_4 > g_3$;
2. Inactivity when $g_4 = g_3$;
3. Left rotation, increasing to a maximum and then diminishing, when $g_3 > g_4 > g_2$
4. Inactivity when $g_4 = g_2$;

5. Right rotation, increasing to a maximum and then diminishing, when $g_2 > g_4 > g_1$;

6. Inactivity when $g_4 = g_1$;

7. Left rotation, increasing when $g_4 < g_1$.

"Thus when one of the groups gradually passes from the maximum to the minimum the sign of the rotation will change four times." [*Three appears to be the correct number*].

We are fully aware of the exceptions to this criterion which led the early investigators to set aside the theory of Guye and of Crum Brown as complete expressions of the relationship between the composition of a molecule and its optical activity. Despite these defects no better method has been devised and the application of this method promises more advance than merely indefinite guesses as to the relationships which may exist. It appears very probable that factors other than the mass of the attached groups may influence the optical rotation of an asymmetric carbon atom; but no one knows what these properties are nor how to evaluate their influence into some other number which might be introduced into some such mathematical expression for rotation as was given by van't Hoff. Levene has proposed his idea in his chapter on Stereochemistry.[1]

"The question of the relationship of chemical structure has been discussed by Levene and Haller, who reached the following general conclusions. The optical rotation of a substance is the resultant of several factors, of which three have been definitely pointed out: first, the respective masses of the radicals attached to the asymmetric carbon atom; the polarity of the groups; and third, the distance of the polar groups from the asymmetric carbon atom. The effect of unsaturation and of branched chains have also been studied but sufficient data have not yet been obtained to warrant general conclusions. It can be said, however, that the influence of the double bond on the optical rotation of normal secondary carbinols depends on its position in the lighter or heavier group and on its distance from the asymmetric carbon atom."

In spite of the addition of these other factors many of the correlations of Levene would be arrived at also by the criterion here suggested so that it appears that, if mass of the groups is not the only factor, it still remains the most important factor governing optical rotation. This does not rule out the possibility that in some cases the effect of polarity or unsaturation or some other factor may not appear and influence the optical rotation. Such an effect would appear to be Fischer's[2] resolutions into active components of propyl, isopropyl cyanacetic acid. The literature indicates that unsaturated groups such as $C=O$, $C=S$, and especially $C=C$ have larger effects on rotatory power than do saturated groups in the same relative position with respect to the asymmetric carbon atom. This is not hard and fast rule for exceptions are known and the $C\equiv C$ bond appears to have less effect than the double bond. It will be shown that the introduction of the phenyl group directly attached to the asymmetric carbon as in mandelic acid has an effect different from that observed in the malic acid series on the one hand or the beta hydroxy butyric acid series on the other. Correspondingly the position of the carboxyl group one step removed from the asymmetric carbon atom as in the last acid mentioned brings about different properties from those observed in the malic acid series or the lactic acid series.

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[1] "Annual Survey of American Chemistry," 4, 260 (1928-29).

[2] Fischer and Flatau: Ber., 42, 2981 (1909).

In the second place the applications of the criteria developed by van't Hoff are made more difficult not only by the existence of factors other than mass which have their effect, but also by the varying conditions under which the experimental data which make up the literature of the Walden inversion were gathered. It is now obvious that the course of any replacement reaction will be dependent on three major factors; (the conditions of the reactions such as temperature, concentrations, etc., being selected so as to minimize the racemization which is so likely to occur during such reaction). These factors are: the starting-out material and, to a lesser extent, the product; the reagent added and its relative concentration; and, finally, the solvent medium. Undoubtedly all three of these factors affect the course of the reaction greatly and the present survey can only make the implicit assumption (made by all other students of the phenomena) that the reactions in question have been carried out under such conditions that the data are really comparable. Thus, to take but one case, the reaction between the amino acids and nitrous acid has in general been carried out under practically the same conditions each time, since they are the only conditions in which we know the reaction to proceed. We know, however, in such a simple case as this appears to be, that the effect of decreasing the acidity of the reaction medium has a marked effect on the mixture of malic acids produced. This has been shown recently by Holmberg[1] who investigated the diazotization of natural dextrorotatory aspartic acid to give natural levorotatory malic acid. By adding increasing amounts of nitric acid the acidity of the solution was increased while the activity of the malic acid decreased.

Normality of nitric acid	0	0.25	0.50	1.0N
Specific rotation of the malic acid in uranyl nitrate	−40.3°	−54°	−306°	−405°

The first solution was acid only with the acidity of the aspartic acid. The phenomena are exactly comparable with those observed in the hydrolysis of chlorosuccinic acid except that there the observations could be continued beyond the point of neutrality (or the point at which equal amounts of the two forms of malic acid were produced which is certainly not at pH 7). The diazotization cannot be carried out in alkaline solution so far as we know; but, if it could, it seems quite probable that dextrorotatory malic acid would be the product in increasing proportions as the alkalinity is increased. Holmberg remarks merely that at the lower hydrogen ion concentrations another reaction mechanism enters which give rise to dextrorotatory malic acid or racemic malic acid. The latter was not the case in the hydrolysis experiments and does not now appear reasonable. In comparison with Holmberg's best value −436° for malic acid under such conditions, the N HNO_3 system gave a product which is about 96% l-malic while that obtained without the addition of nitric acid is 55% l-malic and 45% d-malic acids. The complications entering into this reaction, probably one of the most simple reactions used in studying the Walden inversion, show the need for caution in accepting all the published results as comparable. We[1] have already shown the character of the similar complications in the hydrolysis of chlorosuccinic acid, where hydrolysis in acid solution produces a malic acid of the same sign of rotation as the original chlorosuccinic acid while alkaline hydrolysis gives a malic acid of the opposite sign. Probably the mystery of the Walden inversion will not be fully cleared until we are able to work with data that were obtained under strictly comparable conditions since many of the reactions used are far more troublesome than the diazotization discussed above. The racemization which accompanies nearly every such reaction betrays the existence of a reaction mechanism opposite to that of the principal one, and, which mechanism shall predominate will depend on several factors, the most important of which appears to be the added reagent in most cases.

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[1] Holmberg: Ber., **61**, 1893 (1928).

The applications of the van't Hoff criteria to the reactions of the Walden inversion are somewhat hampered by the fact that the relative amounts of reagent and starting-out material have an effect in some cases. Thus in the discussion of the hydrolysis of chlorosuccinic acid above referred to we have shown that a deficiency of silver oxide leads to one type of malic acid while the presence of more than the equivalent amount of silver oxide favors the formation of the opposite malic acid. In this particular case we consider that the acidity of the medium in which the reaction takes place is the deciding factor, the presence of more silver oxide favoring the alkaline solution reaction because a larger portion of the hydrolysis takes place at the surface of the suspended oxide. But it appears quite possible that the relative amounts of the substances employed may be decisive factors in some of the common reactions employed. The present paper therefore can classify the reagents on the assumption that comparable conditions were observed in this respect too. This classification will then indicate that under the conditions commonly employed these reagents produce Walden inversions while those do not. A justification of the classification is that it shows that the reactions of two similar groups of compounds, the malic acid and the lactic acid series behave alike in that the same reagents fall into the same classes in both series of compounds. In the latter series of compounds differences of composition, particularly the presence of the phenyl group make the classification different but not less sharp. This, then, supports the contention that the added reagent alone does not determine the course of the reactions but that the properties of the starting-out material may be such as to influence the mechanism of the replacement process.

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[1] Bancroft and Davis: J. Phys. Chem., 35, 1253 (1931).

The Application of These Criteria

In the application of these criteria there will in general be three steps to be taken. In the first place the actual rotations of the compounds studied and the conditions under which the rotations were observed must be definitely known. This is especially true of the alpha hydroxy and alpha amino acids and in these cases, only the rotations of the alkali salts or of the esters may be taken as representing authentically the rotation of the actual substance. Secondly, since we are here studying the effects of the varying reagents added, the conditions under which the reactions proceed and especially the relative amounts of reagents involved must be known. Thus the mere statement that a given halogen acid was hydrolyzed in the presence of silver oxide is not sufficient, for we know that a deficiency of silver oxide brings one result while a sufficient excess of silver oxide may produce exactly the opposite product. Finally the relation between the group weights must be considered. This will indicate whether or not direct replacement by the entering group will produce a change in the sign of rotation. This may be shown best by a concrete illustration from the malic acid system. In this compound the groups attached to the asymmetric carbon atom and their respective weights are;

H	OH	COOH	CH_2COOH
1	17	45	59

If the hydroxyl group be replaced by some other group such as NH_2 = 16, or Cl = 35.5, whose weight lies between 1 and 45, we should expect no change of sign on direct replacement. If change of sign results, it indicates that the replacement is not direct but is attended by a Walden inversion. But if the entering group be between 45 and 59, direct replacement will be accompanied by a change in sign and in this case the retention of the sign of rotation of the original compound will show a Walden inversion. Finally, if the hydroxyl group of the original malic acid be replaced directly by a group whose weight is greater than 59, such as Br = 80 or I = 127, the resultant compound will again have the same sign of rotation as that of the original malic acid and again a change of sign will indicate a Walden inversion. In the direct replacement criterion in this last case, it is as though the change in the group weight were sufficient to bring about two reversals of the sign (each time the group weight became equal to 45 and 59 respectively) and these two reversals neutralize each other, the final result being the same sign of rotation as the original hydroxy acid.

We are now in a position to apply these criteria to the more common examples of the Walden inversion. The first one to be worked out and still the best known one is that of the derivatives of succinic acid. We employ the chart given by Walden and find that the designations there given are the proper ones to employ. This constitutes no problem for the chlorosuccinic acids which in all dilutions in aqueous solutions show a nearly constant rotation which is the same as that of the salts and esters. In the same way there is general agreement as to just which acid is l-malic acid and this has been discussed above. The aspartic acid offers more need for caution. Natural asparagine, on boiling with hydrochloric acid, gives an aspartic acid which is dextro-rotatory (about +5°) in aqueous solution and in acid solution, but which in alkaline solutions is levorotatory and which in the forms of its esters is likewise levorotatory. This aspartic acid should therefore be called l-aspartic and is the acid which with NOCl gives levorotatory chlorosuccinic acid and with nitrous acid gives l-malic acid. It would appear quite reasonable that this last reaction should proceed without inversion for one would expect the replacement of the NH_2 (=16) group by the OH (=17) group, in view also of the chemical similarities of the groups, to produce a compound of just about the same optical rotatory power and direction. The rotatory power of the two compounds is just about the same and the retention of the same sign of rotation lends support to the conclusion that no Walden inversion takes place in the reaction. Now this chart shows the interrelation of the amino, hydroxy, and chloro compounds and the application of the method above shows that the weights of all these groups fall between 1 and 45 so that we conclude that in normal replacement, all these compounds of the same sign have the same configuration. Change of sign will therefore indicate abnormal replacement. These same considerations apply also to the bromo or iodosuccinic acids. We find therefore that in the malic acid series;

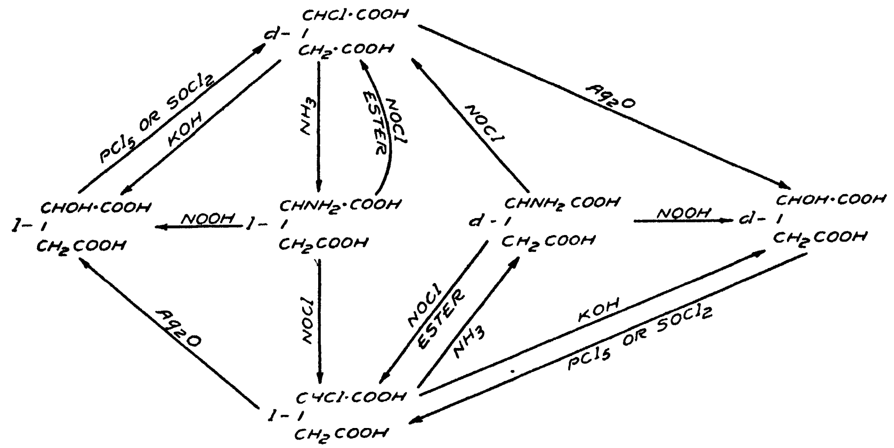

Fig. 1
Malic Acid

Normal reagents are; HNO_2, Ag_2O, NOCl.

Abnormal reagents are, PCl_5, $SOCl_2$, KOH, NH_3.

In this first example it is found that the amino acids and their esters appear to work oppositely toward nitrosylchloride. In the case of the amino ester the group weights are;

H	NH_2	$COOC_2H_5$	$CH_2COOC_2H_5$
1	16	73	87

Replacement of the amino group by the chlorine atom will not change the order of group weights any more than it did in the acid and we should predict no change in the sign of the rotation. That a change in the sign of rotation results from the action of nitrosyl chloride on the ester indicates that there a Walden inversion takes place. This may be attributed to the lesser acidity of the ester or, what seems more probable, to the effect of the ring or lactone structure involving the NH group, just as malic acid has been shown to have such a structure involving the oxygen ring. In the free acid or in the presence of other acids this "lactide" ring is present and by virtue of its more rigid stabilizing power is able to force direct replacement while in the esters the lack of such a ring permits the principal action to be one of abnormal replacement.

The second common example of the Walden inversion that has been investigated is the lactic acid series. In this series both the lactic acid and the amino acid, alanine, possess rotations in aqueous solutions or acid solutions opposite to the rotations of their alkaline solutions or esters and no end of confusion has arisen in the literature on this point. This has been particularly the case when lactic acid was compared to some other compound with a view to establishing configurational relationships. A recent example of this was the reply of Clough[1] to a criticism by Levene. Levene and Haller had claimed as a result of their reactions that an optically active form of 2-hydroxybutyric acid, $CH_3 \cdot CH_2 \cdot CH(OH) \cdot COOH$, which is dextrorotatory in aqueous solution at ordinary temperatures but which yields levorotatory salts and esters, possesses the same configuration as d-lactic acid or l-tartaric acid. Levene and Haller called this the dextro acid, which is of course the wrong designation, and they then pointed out that Clough had reached opposite conclusions to their own. Clough protests that he agrees with their conclusion but not with their designation, and continues: "In order to distinguish the enantiomorphus forms of a compound from one another, the conventional symbols d and l have been assigned to them in a somewhat arbitrary manner. Thus d-lactic acid is the form which is dextrorotatory in aqueous solution at ordinary temperature but which gives rise to levorotatory salts and esters, while l-aspartic acid which may be prepared from natural l-asparagine, is dextrorotatory in aqueous solution. Guye and Jordan who resolved 2-hydroxybutyric acid into its optically active forms, termed that variety of this acid, the salts and esters of which were levorotatory, "*l'acide alpha-oxybutyric gauche*". Beilstein refers to the same compound as "*l-alpha-oxybuttersaure*". The present author also designated this compound l-alpha-hydroxybutyric acid and expressed the view that it was configurationally related to l-tartaric acid." In view of the criteria outlined by van't Hoff and applied in this paper we see at once that there is no real difference of opinion here and, if the lactic acid in question be given its true designation as l-lactic acid, true agreement is arrived at.

Walden[2] is clear on this point for he says: "For the optical designation of the active lactic acids we will indicate that acid whose salts and esters are levorotatory as l-lactic acid. Sarcolactic acid produces levorotatory salts and esters and is therefore designated as l-lactic acid." The reasons given for this view are essentially those of van't Hoff and need not here be repeated. Suffice it to say that in the chart, Fig. 2, Walden gives the lactic acids the proper designations.

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[1] Clough: J. Biol. Chem., 75, 489 (1927).

[2] Walden: "Optische Umkehrerscheinungen," 48 (1919).

This is not the case with alanine, although exactly the same considerations apply as were applied to the hydroxy acid. A sample of alanine whose hydrochloric acid solution showed [a] = 9.4° and whose esters and salts are levorotatory gave on treatment with nitrous acid a lactic acid whose zinc salt showed [a] = −8.0°. This alanine should therefore be known as l-alanine and the action of nitrous acid produced l-lactic acid exactly as in the case of the conversion of l-aspartic acid into l-malic acid. In using these letters thus for these compounds we have reference to the real rotation of the acid in question when that rotation is no longer influenced by any type of anhydride formation or condensation, and not to the actual rotation observed in water alone or under some other incidental condition. The rotation of alanine is so small that it is not recorded; practically always it is converted to its hydrochloride or hydrochlorate and observed thus. It is clear that such rotations are in the opposite direction to the true designation of the alanine studied.

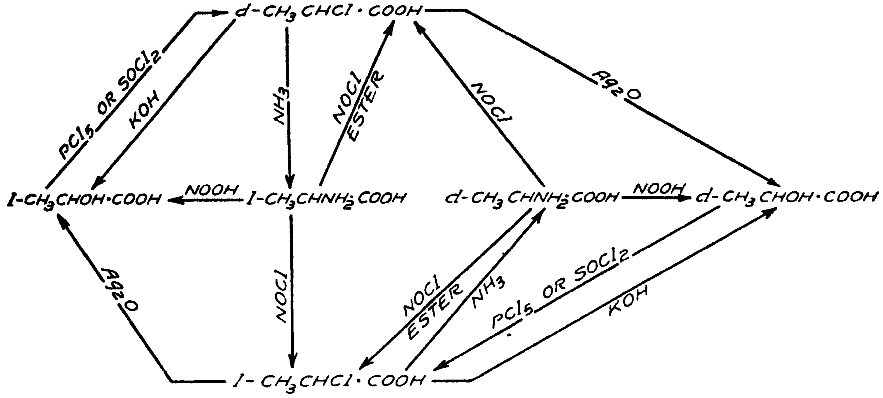


FIG. 2
Lactic Acid

The group weights in the lactic acid series are:

H	CH_3	OH	COOH
1	15	17	45.

Therefore, as in the malic acid series, the amino, chloro, and hydroxy compounds having the same sign will also have the same configuration, and again, after the proper designations are assigned, change of sign indicates a Walden inversion. In this series the reagents are;

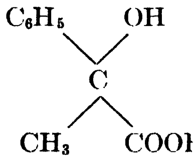
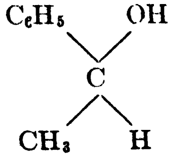
Normal: HNO_2, Ag_2O, NOCl.

Abnormal reagents are: PCl_5, $SOCl_2$, KOH, NH_3.

Comparison of the reagent classes in the lactic and the malic acid systems will show that they are identical. This is as it should be if our criteria are reliable, for the same reagents on such similar compounds should produce or be free from inversion on both compounds and we find this to be the case. As these criteria are applied to other series of compounds, the influence of the various compounds becomes felt, so that a reagent which proved normal in the two systems above may produce inversion in other systems. We have not as yet been able to work out methods for predicting definitely the course of a reaction in a given case but it appears that the presence of phenyl groups in the molecule and the relative position of the asymmetric carbon with respect to the carboxyl group, as well as the character of the groups attached to the asymmetric carbon atom all have their effects on the course of the reaction with a given added substance. Our purpose here is to enable the detection of a Walden inversion when one has taken place in order that subsequent study may be then directed to the finding out why the inversion took place.

Without going into the details of the applications we here present the results of applying these criteria to the principal systems selected by Walden for inclusion in his latest book (1929). In this table I means that the reaction indicated is accompanied by inversion, while N shows that normal replacement takes place.

TABLE I

System	HNO_2	Ag_2O	NOCl	PCl_5	$SOCl_2$	KOH	NH_3
Malic acid $COOH·CH_2·CH(OH)·COOH$	N	N	N	I	I	I	I
Lactic acid $CH_3·CH(OH)·COOH$	N	N	N	I	I	I	I
beta-hydroxybutyric acid $CH_3·CH(OH)·CH_2·COOH$	I	I	I	I			
Mandelic acid $C_6H_5·CH(OH)·COOH$	I	I	I	I	N	N	I
alpha-hydroxy-alpha-phenyl-propionic 	I	I		I	N		
beta-hydroxy-beta-phenyl-propionic $C_6H_5·CH(OH)·CH_2·COOH$	I	I	I	I	N		
Phenylmethylcarbinol 	I	I	N	I	N	I	

The data in this table are not so nearly comparable as could be wished, chiefly because the need of control of reactions and of more definite attention to the relative amounts of substances reacting has not been recognized by the people who made the observations. We may select a single instance to make this clear. The work on the beta-hydroxybutyric acid was done by Fischer and Scheibler[1] who showed that the hydrolysis of the chloro acid to the hydroxy acid in presence of silver oxide went with a change of sign, which applying the criteria, indicated an inversion. This is opposite to the behavior in the case of lactic and malic acids and it was of interest to know if the existence of the beta-hydroxy asymmetric carbon atom group was responsible for the change. This idea did not prove correct for it was found that the reaction proceeded in the presence of four equivalents of silver oxide per mol of chloro acid. As we have shown in the malic acid series, a far smaller excess than this is sufficient to give the same effect as a strongly alkaline hydrolysis with the oppositely rotatory product to that usually obtained in the presence of a deficient amount of silver oxide. In most of the tables of the Walden inversion, the action of silver oxide reported is that of a deficiency of silver oxide, and, in the case of the malic acid series, is a normal replacement, while an excess of silver oxide brings about a Walden inversion. It is probable that this is true also of beta-chlorobutyric acid and that the action of silver oxide on this acid also should be listed as normal. Since no data are available for the hydrolysis of this acid in the presence of deficient silver oxide, this point can not be proved conclusively. It should prove possible in a few years to prepare such a table as this with some assurance that the data are really comparable. By that time we may be able to evaluate the forces which direct these reactions in such a way as to show more rigid correlation between the reagents used and their effects than is now possible.

For the present, we might make a few observations on the table as it stands. The identity of the reactions in the lactic acid and malic acid series is to be expected from the similarities of the compounds themselves and may serve as confirmation of the existence of similar anhydride-type compounds in both series. On the other hand the evidence above indicates that the beta-hydroxybutyric acid is like malic acid in respect to the silver oxide hydrolysis; but in this case a distinctly acid hydrolysis produced the same effect as the excess silver oxide. For the present no conclusions can be drawn, for it may appear that both beta- and alpha-hydroxycompounds react similarly. It does appear that the beta-ring is broken more easily and such compounds are more prone to inversion. Finally the introduction of the phenyl group directly attached to the asymmetric carbon atom induces a complete change in the reaction process, only phosphorus pentachloride retaining its power of inversion through the whole series. At the same time thionyl chloride substitutes directly in such compounds while nitrosylchloride is able to do so on the carbinol where the acidity is low. This effect of the phenyl group has been noted recently by Kenyon, Lipscomb, and

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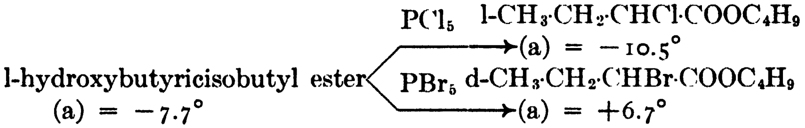
[1] Fischer and Scheibler: Ber., 42, 1227 (1909).

Phillips[1] who report that although thionyl chloride on the hydroxy acids and esters produces compounds of the opposite rotatory power as has been discussed here for malic acid and lactic acid, the products of the same reaction when the compounds used have a phenyl group directly attached to the asymmetric carbon atom are chloro acids and esters of the same sign of rotation as the original hydroxy acid. If however the ester such as ethyl mandelate is dissolved in a tertiary base (pyridine, quinoline, isoquinoline) the action of $SOCl_2$ again produces a chloro compound of the opposite sign to that of the hydroxy acid. They conclude: "There can be little doubt that the mechanism of the interaction of $SOCl_2$ with hydroxy-compounds is modified by the presence of a tertiary base. The work now described suggests, however, that such modification only determines the sign of rotation of the resulting chloro-compound when a phenyl group is directly attached to the asymmetric carbon atom."

Another interesting confirmation of the criteria here offered and a guide to their application is found in the action of PCl_5 and PBr_5 on alpha-hydroxybutyric acid. Walden[2] gives the data and remarks that it is surprising to find that these reagents produce halogen esters of the opposite sign.



$$\begin{tikzcd} & \text{l-}CH_3{\cdot}CH_2{\cdot}CHCl{\cdot}COOC_4H_9 \;\; (a) = -10.5^\circ \\ \text{l-hydroxybutyricisobutyl ester} \;\; (a) = -7.7^\circ \arrow[ur, "PCl_5"] \arrow[dr, "PBr_5"'] & \\ & \text{d-}CH_3{\cdot}CH_2{\cdot}CHBr{\cdot}COOC_4H_9 \;\; (a) = +6.7^\circ \end{tikzcd}$$

The groups in the free acid are;	H	OH	CH_3CH_2	COOH
	1	17	29	45

and it is obvious that the substitution of Cl for OH will change the position of that group by one step with a resultant change of sign. But since PCl_5 is, so far as we now know, always an inverting reagent, this reaction should proceed without change of sign, as it does. But the introduction of bromine involves a double change in the weight position and should result on normal replacement in no change of sign. Now PBr_5 is sufficiently like PCl_5 that we should expect it also to be an inverting reagent and to produce the change of sign which is actually observed. The opposite sign of the products is therefore clearly a result of the relation between the masses of the groups attached to the asymmetric carbon atom, the two halogen compounds having the same configuration, which is opposite to the configuration of the hydroxy acid.

This has been worked out on the basis of the acid group weights and would not follow if the ester weight were introduced. This, therefore, raises the question as to whether the acid ought not always to be taken as the norm for calculation. In all but very rare exceptions the rotations of the esters are in the same direction as the true rotation of the acid even though the group weights may have changed in order. By strict application of the group weight relation, methyl lactate ought to work oppositely in the presence of PCl_5 and PBr_5, but it does not. These considerations indicate that here is an example where the chemical character of the attached group, in this case the carboxyl group, is a more powerful determinant than the group weights alone, and that the criteria are still valid if properly applied to the free acids. The reactions above will surely produce the same divergent results if the free acids are used instead of the esters.

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[1] Kenyon, Lipscomb, and Phillips: J. Chem. Soc., **1930**, 415.

[2] Walden: "Optische Umkehrerscheinungen," 59 (1919).

The Relation of Some Common Hydroxy Acids

It has now been shown how the criteria developed above may be used to correlate the configurations and rotations of the acids which may be converted into one another by simple reactions. These same criteria will also make clear the relationships existing between the various series themselves. For convenience we select the natural lactic acid as the standard of comparison. It has already been shown above that this acid, although dextrorotatory itself, belongs to the levorotatory class, because of the levorotation of its salts and esters. For purposes of comparison with other acids and to make its character clear we shall designate this the l (+) lactic acid and shall indicate the other related hydroxy acids which are of the same configuration.

In this Table II the column headed Relation shows how the criteria were applied. Thus glyceric acid might be regarded as having been obtained from lactic acid by replacing the CH_3 group by CH_2OH (oxidation?). In doing this, the group change is from between 1 and 17 to between 17 and 45. This represents one change and normal replacement would be accompanied by a change in the sign of rotation—it always being insisted that we are dealing with real rotations. In mandelic acid the methyl group is replaced by the phenyl group which represents two steps in increase of group weight or two changes of sign, which balance each other and leave the sign unchanged. All the acids in this table have three groups in common with lactic acid and can be compared with that acid directly except beta-hydroxy-beta-phenylpropionic acid which could be compared with malic acid and thus put in the table.

It has been shown earlier in the discussion of the hydroxy acids that Freudenberg and Clough, using their various methods for correlating configurations, have arrived at the same conclusions as are shown in the table with respect to the correlation of l(+) lactic, l(−)mandelic, l(−)malic, and l(−)tartaric acids. They, however, include l(+)glyceric acid as of this same form while the application of these criteria of van't Hoff indicates that d(−)glyceric is configurationally related to the four acids just named. The experimental data are not sufficient to confirm or deny the relationship of the other three acids named in the table. That the criteria are not complete is shown by the fact that the opposite conclusion is reached concerning the alpha-hydroxy-alpha-phenylpropionic acid if it be compared with mandelic acid instead of lactic acid as was done in the table. In view of the agreement with the experimental results it appears that the comparison with lactic acid is the more reliable.

TABLE II

Acid	Groups				Relation	Configuration related
Lactic acid	H	CH_3	OH	COOH	————	l(+)lactic
$CH_3 \cdot CH(OH) \cdot COOH$	1	15	17	45		
Mandelic	H	OH	COOH	C_6H_5	Two changes	l(−)mandelic
$C_6H_5 \cdot CH(OH)\ COOH$	1	17	45	77	Same form	
alpha-hydroxy-alpha--phenylpropionic	CH_3	OH	COOH	C_6H_5	Three changes	d(+)alpha-hydroxy--alpha-phenyl-propionic
$CH_3 \cdot C(C_6H_5)\ (OH) \cdot COOH$	15	17	45	77	Opposite form	
Malic	H	OH	COOH	CH_2COOH	Two changes	l(−)malic
$COOH \cdot CH_2 \cdot CH(OH) \cdot COOH$	1	17	45	59	Same form	
Tartaric	H	OH	COOH	$CHOH \cdot COOH$	Two changes	l(−)tartaric
$COOH \cdot CH(OH) \cdot CH(OH) \cdot COOH$	1	17	45	75	Same form	
beta-hydroxy-beta-phenylpropionic	H	OH	CH_2COOH	C_6H_5	One change	d(+)beta-hydroxy--beta-phenyl-propionic
$C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot COOH$	1	17	59	77	Opposite form	
	(compared with malic acid)					
beta-hydroxybutyric	H	CH_3	OH	CH_2COOH	No change	l(−)beta-hydroxy-butyric
$CH_3 \cdot CH(OH) \cdot CH_2 \cdot COOH$	1	15	17	59	Same form	
Glyceric	H	OH	CH_2OH	COOH	One change	d(−)glyceric
$CH_2OH \cdot CH(OH) \cdot COOH$	1	17	31	45	Opposite form	

Finally it may be pointed out that the conclusions here reached by the application of these relatively simple standards of comparison are, for the lactic and malic acid systems, in every respect identical with those reached by Freudenberg[1] from very extensive work on the optical rotatory power of the acids in question and of their esters and other related compounds. These authors agree with the present paper in the designation of the acids and their configurational relationships, and finally, therefore, in the character of the reaction brought about by each of the reagents discussed in connection with them. Basically apparently Levene would also agree with us in the grouping of dextro-tartaric, dextro-malic, levo-glyceric, and levo-lactic into the d-series. We have already seen that as late as 1927 Levene[2] was somewhat confused on this point so that it seems reasonable to assume that by the designations above he intended to show the rotations of the acids themselves in aqueous solution and not their true character. We know that the salts and esters of levo-glyceric and of levo-lactic acids are dextrorotatory so that these acids should be shown as d(−) glyceric and d(−) lactic acids. We still cannot agree with Levene with respect to the glyceric acid but do so in respect to the other acids. In addition we also do not agree with Levene in respect to the chloroacids, for it appears that in some of the reactions employed to go from one active compound to the other an inversion is by no means impossible.

Conclusions

1. There are no generally accepted methods for the correlation of the optical rotations of organic compounds and their configurations. This is the next important step to be taken in the elucidation of the mysteries of the Walden inversion, for until it is known definitely when an inversion takes place, there is little hope for learning much about why an inversion takes place.

2. The methods previously employed often have the defect of employing reactions which may themselves include Walden inversions and they lead to contradictory results.

3. The correlation of the rotations of the optically active compounds and their configurations is possible by the use of criteria outlined by van't Hoff. These have two principal steps, the first being the ascertaining of the real rotation of the acid as of the same sign as its salts and esters. The second step is the comparison of the mass of the groups attached to the asymmetric atom as the order of these masses is affected by the introduction of different groups.

4. By the aid of the first of these standards one is able to know definitely what relative configuration is possessed by the acid under study. The application of the secona comparison then indicates whether or not a Walden inversion takes place on group replacement. It is pointed out that even in

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[1] Freudenberg and Lux: Ber., **61**, 1083 (1928).

[2] Levene: Chem. Rev., **2**, 179 (1925).

such reactions as esterification and hydrolysis of the ester an inversion may take place although apparently no bond of the asymmetric carbon is affected.

5. The application of these criteria is attended by certain difficulties which include variations of the conditions under which reactions are carried out, variations of the relative quantities of the reagents employed, and the possibility that in some cases factors other than mass may contribute to the general effect.

6. The application of these criteria to the malic and to the lactic acid series shows that l(−)malic, l(−)chlorosuccinic, l(+)aspartic, l(+)lactic, l(+)alanine, and l(−)chloropropionic acids are all of the same configuration. In this designation the signs within the parentheses indicate the actual observed rotations of the acids in water while the l designation for each indicates that each produces levorotatory salts and esters thus showing their true character.

7. With the configurations in each series thus determined, the detection of the Walden inversion is simple. In both of these series the action of HNO_2, Ag_2O (deficient), and NOCl is by direct replacement; while the action of PCl_5, $SOCl_2$, KOH, and NH_3 is characterized by a Walden inversion.

8. These conclusions are exactly in agreement with those of Freudenberg and it appears that this is the first time that one has been able really to compare the effect of a given set of reagents on even two similar compounds series with respect to the Walden inversion. The criteria here proposed may require future amplification or revision but at least these achievements represent an advance.

9. Similar results are shown for the application of these standards to other hydroxy acid series and it is shown that the effect of the reagents named above is not always as it is in the first two series. Apparently the occurrence of the phenyl group in the molecule or the position of the asymmetric carbon in respect to the carboxyl or other group potent in affecting rotations are able to influence also the course of the reactions into which the molecule enters.

10. It is shown that the hydroxy acids themselves can also be correlated by this method and l(+)lactic, l(−)mandelic, l(−)malic and l(−)tartaric acids are shown to be of the same configuration.

11. The facts that varying the acidity of the medium or varying the relative amounts of reagents employed in the reactions here discussed, has been shown to be capable of completely reversing the course of these reactions as indicated by the products, lead to the conclusion that this may be responsible for many of the abnormalities encountered in the application of these criteria and that many of these reactions must be completely reinvestigated in order to find what they really mean.

Cornell University:

THE REACTION BETWEEN ARSENIOUS ACID AND IODINE*

BY HERMAN A. LIEBHAFSKY

For the purpose of obtaining additional evidence on the rate of hydrolysis of iodine, the reaction

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^- \qquad (1)$$

so extensively studied by Roebuck,[1] is being re-investigated in this laboratory. Since the new experimental material is to be combined with the results of a series of investigations[2] not directly related to the Roebuck reaction (Equation 1), it has seemed advisable to present here certain considerations which may enhance in some measure the value of one of the classic investigations in the field of chemical kinetics.

This investigation has become classic because it represents the first complete demonstration of the relation obtaining between chemical kinetics and chemical equilibrium. The validity over a sufficient concentration range of the rate law for the forward reaction, namely

$$-\frac{d(I_3^-)}{dt} = k_3 \frac{(I_3^-)}{(H^+)\,(I^-)^2} (H_3AsO_3) \qquad (2)$$

and of the rate law for the reverse reaction, namely

$$+\frac{d(I_3^-)}{dt} = k_5 (H_3AsO_4)\,(H^+)(I^-), \qquad (3)$$

and the equality obtained in II between the quotient k_3/k_5 and the experimentally measured equilibrium constant, K_6, of Reaction 1, establish definitely the mechanism of the Roebuck reaction. In the concentration range where Equations 2 and 3 were experimentally established, both the forward and the reverse reaction are concerned with the single rate-determining step

$$HIO + H_3AsO_3 = H_3AsO_4 + H^+ + I^-. \qquad (4)$$

(Possible intermediate addition compounds will not be considered here). Equation 2 can be easily interpreted if we assume that the concentration of hypoiodous acid is governed by the relatively rapid equilibrium

$$I_3^- + H_2O \leftrightarrows H^+ + 2I^- + HIO, \qquad (5)$$

which may be regarded as the sum of the equilibria

$$I_3^- \leftrightarrows I_2 + I^- \qquad (6)$$

$$I_2 + H_2O \leftrightarrows H^+ + I^- + HIO \qquad (7)$$

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*Contribution from the Chemical Laboratory of the University of California.

[1] (a) Roebuck: J. Phys. Chem., **6**, 365 (1902); **9**, 727 (1905); these papers will be designated as I and II. See also (b) Bray: **9**, 573 (1905) (c) de Lury: **10**, 423 (1906); (d) Washburn: J. Am. Chem. Soc., **30**, 31 (1908); (e) Washburn and Strachan: **35**, 681 (1913).

[2] Bray and Liebhafsky, and Bray and Caulkins, J. Am. Chem. Soc., **53**, 38, 44 (1931) are the initial papers dealing with these investigations.

Since hypoiodous acid can not be consumed more rapidly in Reaction 4 than it is produced in Reactions 5 and 7, then, if—as Abel appears to have demonstrated—iodine and water react with moderate speed while tri-iodide ion does not hydrolyze directly at all,[1] the rate of hydrolysis of iodine should be the *limiting* rate realized as the concentrations of hydrogen ion and of iodide are decreased.

Roebuck chose to employ mass units rather than concentrations in expressing the experimental results of his rate measurements. The measured value of the equilibrium constant, K_6, in these units and for 1 liter of solution at 0°C. was $1.5(10^5)$; the value calculated from the specific rates is given as $8.6(10^5)$ in I (p. 396) and $1.4(10^5)$ in II (p. 743.). Professor William C. Bray has kindly called to my attention a mistake in calculation, the correction of which brings the value from I likewise into agreement with that experimentally measured for K_6. The mistake results from evaluating k_3 from a measurement of $-dx/dt$ (x is the number of *mass* units of I_3^- in the reaction mixture) for 600 cc. (I, Table XVII) and k_5 from a measurement of $+dx/dt$ for 155 cc. (I, Table XXVIII); the rate constants thus obtained were used directly to calculate K_6. If $-dx/dt$ and $+dx/dt$ for the *same* volume are employed which is of course the only correct procedure), and if the values of the corresponding specific rates are then used to calculate K_6, we shall obtain the correct value for this equilibrium constant. The values of the specific rates, however, will still depend upon the volume assumed for $-dx/dt$ and $+dx/dt$, and the conversion of these values into conventional units can be carried out only if $-dx/dt$ and $+dx/dt$ for 1 liter are used.

Thus the specific rates given in the International Critical Tables VII, p. 150 (Volume VII appeared after the writing of this paper) must be multiplied by 2 if their values in conventional units are to be obtained. This multiplication is necessary because $-dx/dt$ and $+dx/dt$ for a 500 cc. reaction mixture were used in the calculation. The corrected values agree very closely with those of this paper.

If we therefore calculate the values of $-dx/dt$ and $+dx/dt$ from I for 1 liter, and use the corresponding specific rates to calculate K_6 we obtain $K_6 = \frac{4.67(10^{-1})}{2.10(10^{-6})} = 2.2(10^5)$, a value in much better agreement with the experimental results.

We shall now give the values of k_3, k_5 and K_6 for 0°C in the conventional units—rates in mols/liter/min. and concentrations in mols./liter; the constants in these units are designated by k'_3, k'_5, and K'_6.

$$\text{Forward Rate:} \quad -\frac{d(I_3^-)}{dt} = 9.4(10^{-4})(H_3AsO_3)\frac{(I_3^-)}{(I^-)^2(H^+)} \tag{8}$$

$$\text{Reverse Rate:} \quad +\frac{d(I_3^-)}{dt} = 6.3(10^{-3})(H_3AsO_4)(I^-)(H^+) \tag{9}$$

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[1] Abel: Z. physik. Chem., **136**, 161 (1928) gives 0.25 as the specific rate of the iodine hydrolysis.

$$\text{Equilibrium:} \qquad \frac{(H_3AsO_4)(H^+)^2(I^-)^3}{(I_3^-)\,(H_3AsO_3)} = 1.6(10^{-1})^1 \qquad (10)$$

We may mention next a question which must have been uncertain in the time of Roebuck's work (vide I, p. 391)—the question of whether arsenic and arsenious acids, on the one hand, or their various anions on the other, are of primary kinetic importance. A consideration of the first dissociation constants for the acids[2] shows that no appreciable concentration of an anion of either acid can exist at the concentrations of H^+ (generally above .1 N) obtaining in Roebuck's reaction system; any arsenic compound added initially must react with H^+ to give the (practically) undissociated acid. In the absence of definite evidence to the contrary, therefore, it is entirely logical to assume, as Roebuck did, that only the undissociated acids or their addition products are concerned in the rate-determining step.

In the measurement of the forward rate of Reaction 1, Roebuck found it generally impossible to utilize initial concentrations in calculating the rate constant. For the forward reaction the rate during the first interval was usually greater than the rate expected by an amount beyond the experimental error; e.g. in I, Table I, k_1 for the first interval is .028 as compared with an average of .020 for the first part of the experiment. (k_1 is a first-order rate constant defined by Roebuck in I, p. 370). Even larger discrepancies were observed in this laboratory for the more rapid measurements, which were done in the following manner:

To the rest of the reaction mixture in a 125 cc. glass-stoppered flask, 1 cc. of solution containing either the arsenic acid or the iodine was rapidly added and the flask immediately shaken. Initial time was taken by another observer as the time of mixing. After the time interval for such a sample had expired, the reaction was frozen by adding .1 N thiosulfate solution from a burette in such manner that rapid mixing was secured. Final time was taken when about half the thiosulfate had been added. Approximately 1 cc. of this solution was equivalent to all the iodine initially present in a sample; in freezing the reaction, the amount of thiosulfate was so regulated that a small amount of iodine, which could be accurately determined, remained to be titrated. From the iodine consumed in initially identical reaction mixtures

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[1] The experimental values of Roebuck which were used in the above calculations are: $k_3 = .26$(II p. 738); $K_6 = 1.5(10^{+5})$ and $k_3/k_5 = 1.4(10^{+5})$ (II p. 743). K_6 is for a volume of 1 liter while k_3 and k_5 are both for a volume of 500 cc. The transformation from Roebuck's to the conventional units is given by:

$$(A) = 100(I_3^-) \qquad (C) = \frac{100}{3}(I^-) \qquad E = 100(H_3AsO_4)$$

$$(B) = 100(H_3AsO_3) \qquad (D) = \frac{100}{2}(H^+) \qquad x = 100(I_3^-)$$

The calculation for the reverse rate has been made by Bray: Z. physik. Chem., **54**, 463 (1906); the value there given for the specific rate must be multiplied by 1/.12 to complete the correction to a volume of one liter. ($_3k$ on pp. 488 and 489 should be $_5k$).

( ) denotes "concentration of"; all electrolytes except H_3AsO_3 and H_3AsO_4 are assumed to be completely dissociated. (The equilibrium $I^-_3 = I_2 + I^-$ is, of course, assumed to be always established.)

[2] Wood: J. Chem. Soc., **93**, 411 (1908) gives $K = 6(10^{-10})$ for H_3AsO_3, and Luther: Z. Elektrochemie, **13**, 297 (1907) gives $K = 5(10^{-3})$ for H_3AsO_4; both dissociation constants are fr 25°C.

during varying time intervals, rate constants could be evaluated. The two chief difficulties, aside from the discrepancy mentioned above, encountered in an attempt to study Reaction 1 at concentrations where it is very fast, are oxidation of thiosulfate by arsenious acid and slowness in freezing the reaction. The experimental method finally adopted proved satisfactory; the rate of the reaction could be measured with sufficiently accuracy (estimated at ±20 percent) even when the half time was as short as five seconds. For experiments so rapid that only one point can be obtained in the course of the reaction, the above procedure may be modified thus: Add 1 cc. of I_3^- to start the reaction. Run a convenient number (say six) of samples as rapidly as is possible by the above method. Take the average of the time readings and the average of the burette readings as establishing this point. (The minimum time will be approximately 2 seconds). Run the same number of 1 cc. pipettefuls of I_3^- into a flask, titrate, and compute the thiosulfate equivalent to the I_3^- added. From this average initial thiosulfate reading and the average reading corresponding to the one point established during the course of the run, a fairly reliable value of the rate constant may be computed. The values which have been obtained for k_3 from preliminary experiments are in reasonable agreement with those of Roebuck.

In Experiment 1, Table I, 1 cc. of $H_2AsO_3^-$ solution was added to 20 cc. of a tri-iodide solution containing all the acid; in Experiment 2 the same reaction mixture was made up by adding 1 cc. of acid tri-iodide solution to 20 cc. of arsenious acid solution also containing iodide. In the first experiment the concentrations of iodide and of hydrogen ion changed on mixing; in the second, virtually no change in these concentrations took place. From Equation 8 we calculate that a decrease of 0.02 cc. in the volume of thiosulfate solution required for the titration should take place in these experiments during the twenty second interval.

TABLE I

Concentrations in mols/liter (for the reaction system after mixing):
$(H_3AsO_3) = .040$; $(I^-) = .118$; $(I_3^-) = .00375$; $(H^+) = .067$

Time (sec.)	cc. .1 N $Na_2S_2O_3$ equivalent to I_3^- remaining Experiment 1	 Experiment 2
0	1.53	1.44
5	1.28	1.43
10	1.30	——
15	1.29	——
20	1.26	1.41

A plausible explanation of the high rate involves the momentary establishment of a high concentration of HIO in the boundary region which exists between the arsenic and iodine solutions before the two are mixed. Since the former solution contains neither H^+ nor I^-, a shift of the hydrolysis equilibrium for iodine, Equation 7, can produce HIO in an amount sufficient to cause appreciable reaction even before complete mixing takes place. These considerations, if valid, serve to substantiate the mechanism for the oxidation of arsenious acid and to indicate the rapidity with which HIO can be produced by hydrolysis.

Equation 8 may be written

$$\frac{-d(I_3^-)}{dt} = K_1K_2k_3'' \, (H_3AsO_3) \frac{(I_3^-)}{(I^-)^2(H^+)} = k_3'' \, (H_3AsO_3)\,(HIO) \qquad (11)$$

$K_1 = \dfrac{(H^+)(I^-)(HIO)}{(I_2)}$ is the equilibrium constant for the hydrolysis of iodine;

$K_2 = \dfrac{(I_2)(I^-)}{(I_3^-)}$, the dissociation constant of tri-iodide ion; and k_3'', the true specific rate of the rate-determining step if this step is the bimolecular Reaction 4. For k_3'' as calculated from the value $k_3' = 9.4(10^{-4})$ in Equation 8, we obtain for k_3'' at 0°C. an extremely large value, $1.45(10^{14})$,[1] equal in order of magnitude to the number of collisions we should expect for many bimolecular reactions. Reaction 4 is thus probably the fastest bimolecular reaction for which a rate constant has been accurately measured; the magnitude of this specific rate is the more surprising since neither of the reacting species is ionic. k_3'', for example, is greater by many powers of ten than the specific rate for the oxidation of hydrogen peroxide by hypobromous acid,[2] and those for the oxidation of certain inorganic compounds by bromine.[3] Since the equilibria 6 and 7 are always maintained in Roebuck's reaction system, then, to obtain the heat of activation for Reaction 4, the heat change calculated directly from the temperature coefficient of k_3' must be diminished by ΔH_1 and by ΔH_2, the heats of reaction calculated from the temperature coefficients of K_1 and K_2. Roebuck gives 3.5 as the temperature coefficient of k_3' between 0°C. and 10°C. (I p. 381); the corresponding heat change is +19,300 calories. For ΔH_1 we calculate the value +22,700 calories; for ΔH_2, +4320 calories. For the heat of activation of Reaction 4 we have, therefore, the unexpected value $Q = -7{,}700$ calories; from this figure we find that the rate of Reaction 4 at 10°C. is approximately three-fourths its rate at 0°C. Since Roebuck has obtained agreement between the temperature coefficient of the equilibrium (Equation 1), as calculated from the temperature coefficients of the specific rates, and the equilibrium temperature coefficient as experimentally measured, a serious error in the value 3.5 employed above would seem unlikely. The values of K_1, however, can be regarded only as approximate because of difficulties in the measurement and in the interpretation of the very low conductivities involved in the determination of this constant; but, since the arithmetical value of Q is over one-third that of ΔH_1, we shall consider a negative temperature coefficient for the reaction between hypoiodous acid and arsenious acid as reasonably well established.

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[1] Those values of equilibrium constants at different temperatures, which were used in calculating specific rates and heats of reaction, are:

$K_1 = 3(10^{-13})$ at 25°C.; Bray: J. Am. Chem. Soc., **32**, 914 (1910).
$K_1 = 9(10^{-15})$ at 0°C.; Jones: J. Am. Chem. Soc., **37**, 24 (1915).
$K_2 = 1.40(10^{-3})$ at 25°C.
and $K_2 = 7.2(10^{-4})$ at 0°C.; Jones and Kaplan: J. Am. Chem. Soc., **50**, 1845 (1928).

[2] Bray and Livingston: J. Am. Chem. Soc., **45**, 1251 (1923), give $6.7(10^6)$ as the specific rate for the oxidation of hydrogen peroxide by hypobromous acid.

[3] Francis: J. Am. Chem. Soc., **48**, 655 (1926), has shown that ten inorganic compounds, among them titanous chloride, sodium arsenite, sodium bisulfite and stannous chloride have specific rates for oxidation by bromine in aqueous solution varying from 10^4 to 10^8 in order of magnitude at 25°C.

For the negative temperature coefficient of the third-order reaction between nitric oxide and oxygen, there have been advanced three not entirely unrelated types of explanations; one of these[1] involves the decrease in duration of collisions which takes place as the temperature increases; another[2] accounts for the negative temperature coefficient on the basis of clustering caused by the van der Waals forces; and the third[3] assumes an exothermic intermediate product in equilibrium with the reactants. Of these explanations, only the last seems applicable to a negative temperature coefficient as large as the one for our reaction. To explain it we assume

$$\text{Equilibrium: } HIO + H_3AsO_3 \rightleftarrows H_4AsIO_4;\ \Delta H = -8{,}000 \text{ calories (approximately)} \qquad (12)$$

$$\text{Rate-determining: } H_4AsIO_4 \longrightarrow H^+ + I^- + H_3AsO_4 \qquad (13)$$

This mechanism must be regarded as tentative until the negative temperature coefficient has been established beyond question by a more accurate determination of ΔH_1 and by a measurement of the rate of the forward reaction over a larger temperature range. Rate measurements at the higher temperatures can be done most conveniently by the experimental method outlined in this paper.

In a bimolecular reaction with a specific rate at ordinary temperatures as large as k_3'', practically every collision between molecules of the reacting species must be effective; in other words, such a reaction must have a heat of activation very nearly equal to zero. Using an equation given by Tolman,[4] we may calculate the molecular diameter which must be assumed for a bimolecular gas reaction proceeding with a specific rate of $1.45(10^{14})$ and zero heat of activation. The result, $\sigma = 2(10^{-7})$ cm., is in rough agreement with the value obtained from a similar calculation in another aqueous reaction system.[5] If the rate-determining step in Reaction 1 is the unimolecular Reaction 13, then this value of σ is the smallest which can be assumed for our reaction system; for the bimolecular reaction forming H_4AsIO_4 must be proceeding at a rate even greater than that corresponding to k_3'' as calculated if the equilibrium (Equation 12) is to be maintained. The specific rate of Reaction 13 cannot be calculated definitely; it is probably very large also. A reaction similar in many respects to the oxidation of H_3AsO_3 by iodine is the oxidation of hydrogen peroxide by that same substance. Without discussing here the complexities of the latter reaction system, we may briefly mention that certain preliminary experiments have indicated the possibility of studying this reaction at different temperatures with the hydrolysis equilibrium of iodine (practically) established and the single rate-determining step

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[1] Bodenstein: Z. physik. Chem., **100**, 68 (1922).

[2] Kassel: J. Phys. Chem., **34**, 1777 (1930).

[3] Trautz and Schueter: Z. anorg. allgem. Chem., **136**, 1 (1924).

[4] Tolman: "Statistical Mechanics etc." 242 (1927), equation (543); No. of mols colliding/cc./sec. $= \left[10^{28.4427}\ C_1C_2.\ \sigma^2\sqrt{T\frac{M_1+M_2}{M_1M_2}}\right]$; C_1 and C_2 are concentrations in mols/cc.; σ is the average diameter of the colliding molecules, T the absolute temperature, and M_1 and M_2 are the ordinary molecular weights. This total number of mols colliding is equated to the experimentally measured rate; the equation is solved for σ. Orientation factors and effect of solvent on the number of collisions are not considered.

[5] The other reaction for which such calculation was made is the reduction of iodate ion by hydrogen peroxide. Liebhafsky: J. Am. Chem. Soc., **53**, 896 (1931).

$$HIO + H_2O_2 \longrightarrow H^+ + I^- + O_2 + H_2O. \qquad (14)$$

If this reaction can be isolated, comparison of the resulting data with those for the arsenious acid case should prove interesting.

Calculations of the kind we have just outlined should advance the knowledge of the more intimate mechanisms of reactions in solution. Such calculations employing the extensive data already existing should be valuable first of all in establishing empirically the relation between the number of collisions in solution and the number in a gas; or stated in another way, they should indicate what collisional diameter must be assumed in order that quantitative application of the Arrhenius hypothesis to aqueous reaction systems can be made. If such a diameter is found to be rather widely applicable, it may be generally used to calculate plausible values for heats of activation. Between reactants and resultants in a chemical reaction there must always be an intermediate addition product of short, but indeterminate, life. If the calculated and the measured values of the heats of activation agree, we should conclude that our rate measurements were concerned with the rate of formation of this intermediate complex; and if not, that they were concerned with its rate of disappearance.

We may mention finally that Roebuck established the kinetics of the reverse reaction only in dilute solution: as hydrogen ion and iodide ion concentrations are increased, the simple rate law (Equation 9) is no longer valid; and the reaction tends to become second order with respect to each of these substances. In the absence of more comprehensive experimental evidence, we shall not advance an explanation. It seems probable, however, that a re-investigation of this reaction, employing perchloric instead of sulfuric acid as a source of hydrogen ion, will show, after salt effect corrections have been made, that the increase in order with respect to hydrogen ion is related to the similar increase for iodide.

Summary

An examination, incidental to a re-investigation of the Roebuck reaction, of the original experimental results has yielded some interesting conclusions, which have been presented here. An initial discrepancy in experiments on the forward reaction has been eliminated and explained.

Berkeley, California,
January 6, 1931.

THE WATER CONTENT OF BENZENE

BY ALAN W. C. MENZIES

Studies of the degree to which intensive desiccation affects the physical properties of substances have led to results which are notoriously discordant.[1] Vapor pressure of a desiccated substance has not infrequently been selected for study in preference to other properties as yielding results that are perhaps least equivocal. The earliest publication on this phase of the subject was that of Smith and Menzies[2] on dried calomel; while the latest is at present the interesting work of Greer[3] who studied especially benzene below 50.6°.

It was shown by Greer that the small quantity of water present in a sample of benzene that had been distilled from phosphorus pentoxide within a closed glass apparatus was sufficient to raise the total vapor pressure by several millimeters of mercury higher than that of another portion of the same benzene dried by silica gel. So many precautions were taken to avoid the presence of water that the impression remains that the benzene sample of higher total pressure must itself have been typical of very well dried benzene. We believe, however, that very much drier benzene can readily be obtained, and studied in a glass apparatus, with far fewer precautions. If this is so, the other workers in this field may after all have operated on benzene samples which were initially so well dried that Greer's explanation of their anomalous findings would be inapplicable.

1. In 1910, Menzies[4] had shown that the boiling point of benzene dried over sodium is found by static and dynamic methods respectively with values identical within 0.001°. It might, however, be argued that any abnormal behavior, due to water if present, would be identical for the two methods.

2. More recently, Wright and Menzies[5] studied near 80°, by their method of isothermal distillation, samples of benzene dried by sodium and transferred in a dry pipette to a glass apparatus dried without extreme precaution. The change in vapor pressure on distilling off as much as half of the sample did not exceed 0.2 mm. of mercury. It would appear from the experimental work described under (3) below that lowering of vapor pressure due to removal by distillation of dissolved water from benzene must manifest itself before even one-fourth of the liquid has been fractionated off. The amount of water in our sample, therefore, was so small as not to affect the normal boiling point of benzene by over 0.01°, which is the temperature change corresponding to 0.2 mm.

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[1] Much of the literature of this subject may be found cited in the work of J. W. Smith: "The Effects of Moisture on Chemical and Physical Changes" (1929).

[2] Z. physik. Chem., **76**, 713 (1911).

[3] J. Am. Chem. Soc., **52**, 4191 (1930).

[4] J. Am. Chem. Soc., **32**, 1616 (1910).

[5] J. Am. Chem. Soc., **52**, 4699 (1930).

3. In these circumstances, and because other workers in the field of intensive desiccation had studied benzene at 80° and above, it was of interest to find if the vapor pressure of benzene, as customarily handled in the organic laboratory, and near its normal boiling point, was ordinarily affected by the presence of water. For one might anticipate that, on simple distillation and even without the use of a desiccant, any water present in the benzene would pass away with the earliest fractions by reason of its relative richness in the vapor phase. Accordingly, the experiments described below are designed to test the behavior of undried benzene from which a portion has been distilled off.

Method A. The apparatus employed was that devised by Menzies for determination of molecular weights of dissolved substances by direct measurement of vapor pressure lowering of a solvent. A description of this may be found in the original article or elsewhere,[1] but Fig. 1, although drawn to illustrate Method B, will serve to recall the form of the apparatus. About 130 cc. of a good grade of commercial "C.P. crystallizable benzene conforming to the standards of Murray" was charged into the outer bulb A and boiled for ten minutes under reflux. About 15 cc. were then distilled off through the condenser in a non-reflux position, and discarded. The first runnings were cloudy, due to water. The connection D to the condenser was closed, and a further quantity of like volume was distilled off through the gauge tube C and inner tube B, with the object of at least partially removing water adsorbed on the glass walls of these portions of the apparatus. The inner tube was then charged with a portion of the remaining benzene. To remove dissolved gases, the connection to the condenser being closed, benzene vapor was "blown through" the gauge tube and inner tube, which was then closed by stopper E, while the connection to the condenser was simultaneously opened. After thermal equilibrium had been reached, the zero reading of pressure was taken, in terms of mm. of difference of level of the benzene surfaces in the inner tube and the gauge tube. The blowing through process was repeated until the results were constant. (i) Several grams of anhydrous magnesium perchlorate were then added to the inner tube. Difficulty was anticipated in removing adsorbed gases from the large surface offered by this solid, but no such difficulty was experienced. The zero reading obtained, in the manner explained above, was identical, within the experimental error, with that obtained in the absence of the desiccant, and remained constant until the experiment was discontinued after two hours. It may be recalled that readings with this form of apparatus are not affected by slow change of atmospheric pressure.

This result pointed to the essential absence from the benzene of such an amount of water as would affect the vapor pressure of benzene at 80° by so much as half a millimeter of mercury. It may be objected that the efficiency of magnesium perchlorate as a desiccant at 80° is uncertain. (ii) Potassium hydroxide as a desiccant has been studied by Baxter and Starkweather[2] at 50°, at which temperature they found that it is in equilibrium with an aqueous pressure not greater than 0.007 mm. of mercury, although possibly less.

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[1] Cf. Staehler: "Arbeitsmethoden in der anorg. Chemie," 3, 169 (1913).

[2] J. Am. Chem. Soc., 38, 2038 (1916).

Several grams of potassium hydroxide, freshly fused at a red heat and powdered on cooling in a pre-dried hot mortar, were introduced with a fresh sample of benzene treated as formerly, in the same manner as with magnesium perchlorate. After blowing through as before, the same constant zero reading was obtained as in the absence of the desiccant. This points to the same conclusion as in (i).

Method B. It may be objected that these desiccants are, in the presence of benzene, for some reason unable to function, or, at least, do not function in the time allowed. The same disability has indeed been imputed to phosphorus pentoxide in like circumstances. To meet this objection, the dissociation pressure of a salt hydrate pair was measured within the inner tube of the apparatus.

If no vapor is present in the benzene vapor, then the full aqueous pressure furnished by the salts should be found as a quantity additive to the pressure of benzene vapor, but if the benzene vapor already contains some water vapor, the pressure found and measured should be the difference between the true aqueous dissociation pressure of the salts and the partial pressure of water already existant in the benzene vapor before the salts are added.

As a suitable salt hydrate equilibrium to utilize for this purpose was chosen that represented the equation

$$ZnSO_4,\ (NH_4)_2SO_4,\ 6H_2O \leftrightarrows ZnSO_4,\ (NH_4)_2SO_4,\ 2H_2O + 4H_2O.$$

The pressures of this system have been measured in eleven observations by Caven and Ferguson[1] from 30.7° to 79.4°. The double salt is one of those which is readily prepared in a pure condition. At 80°, a pressure over 90 mm. of mercury is to be expected. In order to be able to measure such a high pressure in our apparatus, about 5 cc. of mercury was placed in the inner tube B, as shown in Fig. 1, in addition to the benzene. The manipulation was similar to what has already been described. About 3 grams of salt were employed, obtained by freshly efflorescing the hexahydrate in an air oven at 90° until the water content corresponded to 5.5 H_2O, and subsequently guarding against adsorption of water. Corrections to the increase of pressure observed were necessary (a) for the pressure due to liquid benzene and solid salt resting upon the mercury, and (b) for the density reduction of mercury and benzene at 80° (factors of 13.40 and 0.815 respectively) to mercury at 0°. The value of correction (a) was determined by separate experiments made outside the apparatus with tubes of similar dimensions to those forming part of the apparatus. Equilibrium was reached within an hour, and repetition of the blowing through process yielded concordant results.

The dissociation pressure found was 95.7 mm. at 80.2°. The temperature was known to ±0.1° by use of a certified mercurial thermometer of recently determined zero-point. Assuming as correct the three-constant equation given by Caven and Ferguson to represent their results, ±0.1° corresponds at 80.2° to ±0.5 mm. pressure. Looking also to possible errors in pressure measurement, our value may well be in error by 1 mm. The pressure at 80.2° according to Caven and Ferguson's equation is 96.6 mm., which is 0.9 mm. higher than our value, but within our error of experiment.

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[1] J. Chem. Soc., **125**, 1307 (1924).

A possible source of error not taken into consideration above is the alteration in the vapor pressure of benzene itself by reason of the water now dissolved in it. The amount (expressed as mol fraction) of such water will bear nearly the same ratio to the amount at saturation as its partial pressure does to that of pure water. For benzene saturated with water is in equilibrium, as to partial pressures of the components, with water saturated with benzene, whose aqueous pressure is obviously near that of pure water. The Duhem-Margules relation is not very helpful in evaluating this correction to the partial pressure of benzene, partly owing to lack of data. It may be pointed out that this relation obviously fails to hold in cases such as that of heptane and ethyl alcohol[1] where one of the partial pressure-composition isotherms passes through a maximum. Study of the published partial pressure-composition curves for pairs of non-ideal liquids leads one to anticipate a lowering by water of the partial vapor pressure of benzene much less than 2.8 mm., which is approximately that demanded in this case by Raoult's law. Liquid pairs are known where the partial pressure of the solvent (as ethyl alcohol) is actually raised by the presence of the solute (as heptane). For these reasons, no attempt was made to apply the small and uncertain correction for possible error from this cause. However, it seems unlikely that water present before the introduction of the salts influenced the pressure of the benzene used for the experiment by as much as two mm. of mercury.

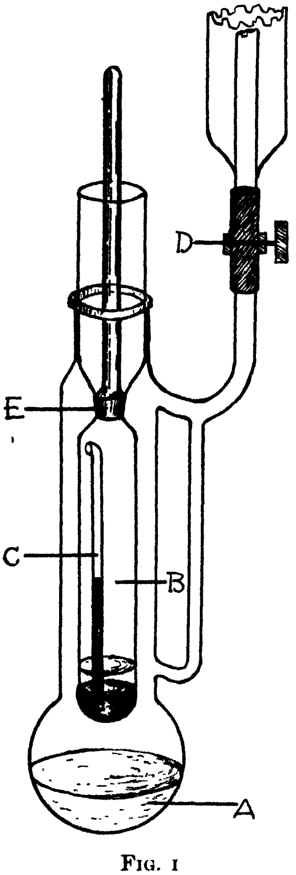

FIG. 1

The utility of the method here employed for measuring dissociation pressures of salt hydrate pairs will be referred to in an article[2] which follows.

Conclusions

From these experiments it would appear that, if ordinary undried benzene be distilled at about 80° and the first one-quarter fraction be rejected, the remaining benzene exhibits a vapor pressure that has suffered alteration from the possible presence of water in an amount not exceeding about 0.2 percent. This corresponds to a change in the normal boiling point of less than 0.1°. Beyond these limits, apparently abnormal vapor pressure results obtained by workers with intensively desiccated benzene cannot be attributed to the water content of their "ordinary" benzene, provided the latter has received even the very simple treatment of partial distillation outlined above.

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[1] Smyth and Engel: J. Am. Chem. Soc., 51, 2660 (1929).

[2] By Menzies and Hitchcock.

Summary

It is pointed out that benzene dried by sodium and transferred to a glass apparatus has been found free from such an amount of water as would alter the normal boiling point by 0.01°.

Two methods have been described for examining the water content of the vapor of benzene at its boiling point.

It is shown that, if one-fourth of a sample of ordinary benzene, containing water, is distilled off at atmospheric pressure, the remainder contains less water than would affect the normal boiling point by 0.1°.

The bearing of this upon work with intensively desiccated benzene is pointed out.

A simple form of indirect method of measuring dissociation pressures of salt hydrates has been described.

Princeton University,
January, 1931.

MISLEADING EQUILIBRIA ENCOUNTERED IN THE MEASUREMENT OF DISSOCIATION PRESSURES IN SALT-HYDRATE SYSTEMS

BY ALAN W. C. MENZIES AND C. S. HITCHCOCK

It is only too obvious to those interested that, while the number of published experimental results in this field increases year by year, there is a regrettably large degree of discordance between the values found by different workers. It is hoped that the present communication may be of use in tending to remedy this unfortunate situation.

The errors caused by the neglect of adsorbed permanent gases which are so difficult to remove from static tensimeters are now better appreciated than in the days of Frowein, faith in whose otherwise excellent results was the cause of much interesting if nugatory speculation as to the cause of the high values yielded by the gas-current saturation method. This difficulty disappeared when it became apparent[1] that the tensimetric results of Frowein in question were themselves too low.

Apparently insignificant points of experimental technique, such as the use of glass wool in an absorption train, have been shown capable[2] of producing considerable discrepancies. Profiting by this and other constructive criticisms offered by Menzies, Partington and Huntingford[3] repeated the earlier work of Partington[4] on the aqueous pressure in equilibrium with the system $CuSO_4$, $5\text{-}3H_2O$ and obtained new values which were markedly higher.

In the present article a rapid method of measurement will be illustrated and shown to be applicable in difficult cases; and examples will be adduced to show that a genuine equilibrium pressure is sometimes reached which, however, is that of the vapor of water merely adsorbed upon the salts rather than an equilibrium dissociation pressure.

Methods. Two methods were employed: (1) the well-known gas current saturation method; and (2) a method whose novelty makes necessary some words of explanation.

It has often been reported that equilibrium between water vapor and a salt hydrate pair is reached more quickly if the two solid phases are in contact with a liquid in which water is at least slightly soluble; and this gain in speed is sought in several of the so-called indirect methods of dissociation pressure measurement which utilize solutions of water in such liquids as ether[5], ethyl alcohol[6] or isoamyl alcohol.[7] After the solid phases have been brought to equilibrium with the liquid, the water concentration and aqueous partial pressure of the latter are then arrived at by independent experiments.

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[1] Cf. Menzies: J. Am. Chem. Soc., **42**, 1951 (1920).

[2] Menzies: J. Am. Chem. Soc., **42**, 978 (1920).

[3] J. Chem. Soc., **123**, 160 (1923).

[4] J. Chem. Soc., **99**, 467 (1911).

[5] Linebarger: Z. physik. Chem., **13**, 500 (1894).

[6] Foote and Scholes: J. Am. Chem. Soc., **33**, 1309 (1911).

[7] Wilson, Noyes and Westbrook: J. Am. Chem. Soc., **43**, 704, 726 (1921).

For the work which follows, we wished to employ such a liquid in the hope of accelerating attainment of equilibrium; but we wished also (a) to be able to follow readily by the eye and without analysis the development of aqueous pressure in the system; and (b) to be able to operate far above room temperatures but without the inconvenience of a cumbersome high temperature tank thermostat. To meet these conditions, we found the method briefly outlined in the preceding article would serve admirably. With this apparatus, also, low pressures may be directly measured in terms of a column of liquid much less dense than mercury.

In general, dissociation pressure equilibria of such salt hydrate pairs as yield only a low pressure are attained only slowly, and it is especially in such cases that the results of different investigators are apt to show discrepancy. For this reason the case following was suitable for study.

1. *$BaCl_2$, 1.8 H_2O in Chloroform.* Equilibrium in the system $BaCl_2$ 2-1 H_2O and vapor is universally reputed to be difficult of attainment.[1] Baxter and Cooper, whose work is the more to be trusted because they were well aware of the difficulties, have measured this dissociation pressure at 15°, 25° and 40°, and the three-constant equation which they fit to these observations yields 56.7 mm. for the pressure at 60.1°, which was the boiling point of chloroform under the existing barometric pressure, as used by us for our method (2).

Our sample of dihydrate, Merck's "reagent" grade, was effloresced in an oven at 55° to a composition $BaCl_2$, $1.8H_2O$. Since the expected pressure would have required a column of chloroform to balance it longer than our apparatus is tall, we employed a few cc. of mercury in the inner tube of the apparatus to serve as the manometric liquid. The manipulation and corrections have already been referred to.[2] The density of chloroform at its normal boiling point was taken as 1.410.

Equilibrium was reached within half an hour, duplicate experiments yielding 57.3 and 57.8 mm. respectively at 60.1°. Our temperature measurement, by a Reichsanstalt certificated thermometer whose zero point had recently been redetermined, is good only to the nearest one-tenth degree. The average of these results, 57.5, may well be in error by one millimeter, and is, therefore, in good agreement with the extrapolated value of Baxter and Cooper.

A correction, 0.3 mm., due to the lowering of the vapor pressure of chloroform within the inner tube by the water dissolved in it may be computed, assuming Raoult's law, from the following data: solubility of water in chloroform at 60°, 0.8 percent,[3] vapor pressure of water saturated with chloroform, about 149 mm. Because information is lacking on the effect of small mol fractions of water on the vapor pressure of chloroform, this correction was not applied, but the calculation serves to show that the value of the true correction is presumably small.

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[1] Cf. Baxter and Cooper: J. Am. Chem. Soc., **146**, 923 (1924); Schumb: **45**, 342 (1923); Partington: J. Chem. Soc., **99**, 49 (1911).

[2] See preceding article J. Phys. Chem., **35**, 1655 (1931).

[3] Extrapolated from values in I. C. T. **3**, 387.

It is evident that, in this case, attainment of the true dissociation pressure presents no difficulty under our experimental conditions. We had guarded against the adsorption of water by the salts in handling, and no ambiguity was likely as to the hydrates present. A more difficult case was accordingly selected.

2. *$CuSO_4$ 1-0 H_2O.* The measurement of the equilibrium pressure for this system has presented such difficulty to various workers that it is not at all obvious what the true p-t relation really is. We have arrived at this in the following manner. The three independent investigations of Bell and Taber,[1] Foote[2] and Crockford and Warrick[3] have reached reasonably concordant values for the concentration of aqueous sulfuric acid with which these two solid phases are simultaneously in equilibrium. If we average these values for 25° we obtain a concentration of sulfuric acid about 87.8 percent. If now we suitably graph against concentration the logarithms of the aqueous pressures over sulfuric acid solutions at 25° as given in International Critical Tables, we find a pressure for 87.8 percent nearly 0.017 mm. of mercury. Siggel,[4] in Nernst's laboratory, in an effort to improve upon the work of Schottky,[5]

TABLE I

Dissociation Pressures in the System $CuSO_4H_2O \leftrightarrows CuSO_4 + H_2O$

Observers	Temp. °K.	Pressure mm. Hg Obs'd.	Calculated Siggel	Calculated M. and H.	Difference in mm. Obs'd minus Calc'd Siggel	Difference in mm. Obs'd minus Calc'd M. and H.
Averaged from three	298.1	0.017	0.019	[0.017]	−0 002	0.0
Siggel	372	6.0	6.04	5.96	−0.04	+0.04
"	383.2	12.0	11.92	11.9	+0.08	+0.1
"	403.9	38.2	37.9	38.6	+0.3	−0.4
"	410.2	53.5	52.7	53.9	+0.8	−0.4
"	420.4	90.4	88.0	90.6	+2.4	−0.2
Average of preceding five values all taken as positive					0.72	0.23
Algebraic sum of the five differences					+3.54	−0.86
Schottky	363.6	4.6		3.46		+1.14
Foote and Scholes	298.1	0.8		0.017		+0.78
Dover and Marden	298.1	1.3		0.017		+1.28
Müller-Erzbach	298.1	0.5		0.017		+0.48

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[1] J. Phys. Chem., 12, 171 (1908).

[2] J. Am. Chem. Soc., 37, 288 (1915).

[3] J. Phys. Chem., 34, 1064 (1930).

[4] Z. Elektrochemie, 19, 340 (1913).

[5] Z. physik. Chem., 64, 415 (1908).

an earlier pupil of Nernst, determined the dissociation pressure of this salt system at five temperatures from 99° to 147.4°. Siggel proposes a three-constant equation to average these results. If, however, using the above datum for 25° and an average of Siggel's data we find the constants in a two-constant equation (E) of the form $\log p = A - B/T$, where A evaluates as 11.040 and B as 3818.2, we are able to average Siggel's results considerably better than he does himself, as is shown in Table I. We have given greater weight to his two lower temperature values, in which Siggel places most trust. To this table we have appended also the values of certain other observers.

The value of Foote and Scholes[1] was obtained indirectly by equilibration with aqueous ethyl alcohol. That of Dover and Marden[2] by the transpiration method, purports to give only the apparent pressure under their experimental conditions.

(a) *Gas Current Method.* Anhydrous cupric sulfate and the monohydrate were obtained by heating the pentahydrate at about 240° and 100° respectively. Approximately equal quantities of the two salts, in granules of an average dimension of four mm., were mixed and charged into two "saturators" tubes each of 5 cm. diameter and 30 cm. length. These were immersed in a thermostat at 40° and connected by ground glass joints with two water absorption tubes containing anhydrous magnesium perchlorate, situated outside the thermostat. The weight of the second of these absorption tubes remained sensibly constant. In all, some 1500 liters of air freed from moisture by means of magnesium perchlorate were passed through the train at this temperature at a rate near 1½ liters per hour, causing the copper salts to lose some 420 mg. of water. The equilibrium pressure expected, according to equation (E), is 0.070 mm. The pressures of water found from the observed gain in weight of the absorption tubes for a metered volume of air ranged from 1.51 mm. progressively downward to 0.08 mm., at which point the bath temperature was raised to 50.0°. At this temperature the anticipated pressure is 0.167 mm. During the passage of 560 liters, the pressure measured decreased from 0.18 smoothly through the dissociation equilibrium value to 0.11 mm. when the experiment was discontinued.

In this instance, the dynamic equilibrium of dissociation is apparently very slow in both directions. During a pause in the work following the experiments at 40°, the saturator tubes had been left closed and inactive at room temperature for three summer months. The aqueous pressure within the tubes, however, remained five-fold higher than the dissociation pressure. At any particular epoch during the course of these experiments, measurements by any static method of the vapor pressure of water as yielded by this material would obviously have given concordant results. But the pressure measured would have been that of adsorbed water and not a true dissociation pressure.

In answer to the question how the copper salts in the saturator tubes acquired the water which they later yielded up as described, at least two replies might be made: (1) that this amount of water in the form of a thin film was in equilibrium with the aqueous pressure in the drying oven at 100°, for example; or (2) that the water was picked up at room temperature from the air of the room during the process of charging the absorption tubes. It must be recalled that the copper salts employed resulted respectively from the removal of 4 or 5 molecules of crystalline water from each "molecule" of pentahydrate of cupric sulfate and that the new specific surface so produced must be very large. A quantity of a few grams of gross analysis $CuSO_4$, 0.9 H_2O was found to gain weight on standing in the balance case containing ordinary room air at the rate of 2 percent per hour.

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[1] J. Am. Chem. Soc., **33**, 1309 (1911).

[2] J. Am. Chem. Soc., **39**, 1609 (1917).

In those cases where the specific surface of the salts is large, where the dissociation pressure to be measured is low and where the rate of the chemical reaction is slow, the opportunity for error due to adsorbed water becomes most favorable.

(b) *$CuSO_4$, 0.9 H_2O, in Benzene.* The solid was prepared by removal of water from the pentahydrate by prolonged heating in a drying oven at 110° and was presumed to be a mixture of $CuSO_4$, H_2O and $CuSO_4$. Adsorption of water during handling was guarded against. At 80°, which is near the normal boiling point of benzene, the expected dissociation pressure for the system is 1.68 mm. of mercury, according to equation (E). The pressure found by method (2), using benzene, was 1.6 $\pm$0.1 mm. This was reached with difficulty within an hour, the speed being increased by shaking and by use of larger quantities of the salts. Otherwise several hours might be consumed.

The error due to the effect of the dissolved water upon the vapor pressure of benzene, computed as indicated in the preceding article, would in this case reach only 0.006 mm., and is therefore negligible.

3. *$CuSO_4$, 2.9 H_2O, by Dehydration, in Chloroform.* The systems composed of vapor and cupric sulfate with five and three and with one and three molecules of water have been studied by Carpenter and Jette[1] in the ranges 25°-90° and 25°-80° respectively. While an examination of their results, which will be discussed elsewhere, points to their lower temperature values for the second system being too high, due, doubtless, to adsorbed water, their values at 60.0°, which by interpolation we find near 83.4 and 58.8 mm. respectively, are probably not far from the truth. As a desirable antecedent to our next experiment, we made two rough trials, using method (2) with chloroform, with a solid of analysis corresponding to $CuSO_4$, 4.5 H_2O, and obtained a dissociation pressure at 60.0° of $80._8 \pm 1.5$ mm. It may be recalled[2] that one molecule percent of the isomorphous sulfates of manganese, zinc and magnesium in solid solution lowers the dissociation pressure of cupric sulfate pentahydrate by 8.6, 6.2 and 2.3 percent respectively. Our copper salts gave negative tests for these and other metals.

.We then prepared a sample of water content corresponding to 2.9 H_2O by allowing another portion of the material used in experiment (2b) to take up water from the air of the laboratory over a period of two days. Using the same method, pressures at 60.0° of 73.2 and 71.0 mm. were obtained in successive experiments, pointing to a slow disappearance of adsorbed water. What is here being measured is clearly not the true equilibrium pressure of either of the systems mentioned, but that of the less hydrated system as vitiated by the presence of adsorbed water whose effect in this case disappears but slowly.

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[1] J. Am. Chem. Soc., **45**, 578 (1923).

[2] Cf. Hollmann: Z. physik. Chem., **37**, 193 (1901).

Summary

1. The method very recently proposed by Menzies is shown to yield, often within an hour, true results for the dissociation pressure of certain salt hydrates, including the difficult cases of $BaCl_2 2H_2O \leftrightarrows BaCl_2H_2O + H_2O$ and $CuSO_4H_2O \leftrightarrows CuSO_4 + H_2O$.

2. A linear equation is proposed by which to represent the pressure-temperature relation in the last-named system.

3. It is shown that, in salt hydrate systems, equilibrium pressures may be attained that are not true dissociation pressures, but rather pressures due to adsorbed water. The incidence of this source of error is discussed.

Princeton University,
January 1931.

A STUDY OF ORGANIC ACID IRON SOLUTIONS*

I. Concentrations and Colors

BY NORMAN J. HARRAR AND FRANK E. E. GERMANN

Introduction

A great variety of substances present in natural waters may act as solvents upon iron minerals. The effects of a number of these have been estimated from natural sources and sometimes tried out under artificial conditions. The solvent effects of organic acids on iron oxides were studied by Harrar[1] and it was shown that the dissolution of iron depended upon the nature of the oxide, the nature of the acid, and the nature of the resulting substance. It was found that a satisfactory explanation of this third factor could not be advanced because the precise nature of these organic iron compounds is a matter of considerable controversy.

The largest and most important contributions to the subject have been made by Weinland and his students,[2] who regard these substances as complex compounds, which dissolve in water with the formation of complex organic iron ions. This view seems to be based largely upon analyses of a great number of crystalline preparations and is supported by the work of other investigators. On the other hand, color comparisons have led Pickering[3] and others to suggest that the properties of these solutions indicate the presence of colloidal particles.

An important application of this distinction is reviewed by Thomas[4] in a recent article on the absorption of iron by plants. He states the conflicting opinions about the form in which iron must exist to be absorbed, suggests a "colloid-solution equilibrium" of

$$\text{"Colloidal } Fe_2O_3.xH_2O \rightleftarrows \text{Dissolved } Fe(OH)_3 \rightleftarrows$$
$$\text{Ionized Fe} \ldots. + 3(OH)^{-}\text{"}$$

and finally concludes that "more facts are needed" before any further progress can be made in that field.

This work had for its purpose, therefore, the collection of more information about the form in which iron exists in organic acid solutions, with particular attention to the possibilities of complex formation and of colloidal properties.

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* Contribution from the Department of Chemistry of the University of Colorado.

[1] N. J. Harrar: Econ. Geol., **24**, 50 (1929).

[2] R. F. Weinland: "Einführung in die Chemie der Komplex-Verbindungen" (1919); Weinland and Reihlen: Ber., **46**, 3144 (1913); Weinland and Paschen: Z. anorg. Chem., **92**, 115 (1915); Weinland and Loebich: **151**, 271 (1926) and many others.

[3] S. U. Pickering: J. Chem. Soc., **103**, 1358 (1913); **105**, 464 (1914); **109**, 235 (1916).

[4] W. Thomas: Soil Science, **27**, 259 (1929).

Plan of Investigation

The solutions of the complex compounds for this study were prepared by dissolving freshly precipitated ferric hydroxide in various organic acids. The quantity of the hydroxide used was an amount calculated to give about one gram of iron in 250 c.c. of solution, although in some cases, not this much could be dissolved. The acids were of normal concentrations, except as solubility limits interfered and forced the use of saturated solutions. Acids of this strength were most convenient for getting the iron into solution, and then any desired concentration could be obtained by dilution.

The selection of the organic acids was first limited to the normal series, beginning with the three simplest monobasic acids: formic, acetic, and propionic and the first four dibasic acids: oxalic, malonic, succinic, and glutaric. Then to study further the relation of dissociation constants, more of the non-substituted type were selected and a wide range of acid strengths covered.

The actual examination of the complexes produced involved a gradual development of methods and criteria to be applied. It was intended that the conclusions reached be based upon comparisons of results from a number of different angles and checked by as many acids as possible. Organic compounds, of course, offer excellent gradations in properties for this kind of work and reasoning.

Preparation of Solutions

The concentration of iron desired was one gram in 250 c.c. of one normal acid solution and it was to be dissolved as freshly precipitated ferric hydroxide. This was accomplished as follows:

A sample of Baker's Analyzed Ferric Oxide was dissolved in hot concentrated HCl, diluted with distilled water and treated with excess NH_4OH. As much water as possible was removed by suction, but it was not otherwise dried. The hydroxide was then transferred to a bottle of about 270 c.c. capacity. The solutions finally obtained were always analyzed for iron and those which did not contain within one-tenth of the required one gram in 250 c.c., were rejected.

The iron in solution was determined by titration against potassium permanganate. The latter was a Mallinckrodt Analyzed Chemical, checked against a Bureau of Standards sodium oxalate (sample no. 40 b). The usual procedure was to treat the solution with sulfuric acid, run it through a Jones Reductor and titrate at once with permanganate. In a few cases, the acid interfered with this titration and it was necessary to evaporate the solution to dryness, char the residue, and redissolve the iron in sulfuric acid.

The acids were all of C.P. grade, most of them Eastman chemicals and the others, Kahlbaum or Mallinckrodt preparations. Those which were sufficiently soluble, were weighed out in amounts calculated to give normal solutions and the others were shaken with distilled water until nearly saturated solutions developed.

These acids were titrated against NaOH, which was checked against a Bureau of Standards benzoic acid (sample no. 39 c) and those of the readily soluble acids which were not within one-tenth of one normal concentration, were remade or rejected.

The acid solution, to the amount of 250 c.c., was added to the bottle containing the freshly prepared ferric hydroxide and the bottle stoppered tightly. It was then vigorously agitated on a shaking machine until the solid had apparently dissolved or until it appeared (after about five or six hours) that the action was practically complete. A short period was allowed for settling and the solution was ready for examination.

Concentrations

The concentrations of iron obtained in the solutions and the strengths of the acids employed are given in Table I. In all cases, preparations and determinations were made in duplicate. The results were checked still further by repeating the entire preparation and examination of each solution.

TABLE I

Acid	$K.10^4$	Normality of Acid	Grams of Fe per 250 c.c.
Formic	2.14	1.008	1.040
Acetic	.18	1.054	.958
Propionic	.14	1.008	.702
Butyric	.15	.782	.411
Oxalic	380.	.990	1.009
Malonic	16.1	.991	.941
Succinic	.66	.968	.498
Glutaric	.47	.985	.204
Adipic	.37	.315	.081
Tricarballylic	2.2	1.020	.156
Maleic	120.	.936	.923
Fumaric	10.	.126	.004
Mesaconic	7.9	.404	.014
Chloracetic	15.5	1.094	.985
Dichloracetic	500.	1.062	.947
Trichloracetic	2000.	1.049	.936
Benzoic	.66	.026	.006
Phenylacetic	.50	.129	.003
Phthalic	12.6	.087	.026
Hydrochloric	—	.976	.917
Sulfuric	—	.962	1.014

In this table the dissociation constants are expressed, for convenient comparison, as times 10^4 and for these values the tables of Landolt-Börnstein[5] and the critical work of Lunden,[6] were consulted. The figures in the last two columns were determined by the methods described above.

The tests applied to some of these solutions were rendered almost worthless by the low solubility of the acid involved or by its poor solvent effect on ferric hydroxide. It will be noted that this is true of the aromatic acids used and of fumaric and mesaconic acids. All the others dissolved at least enough iron to make possible the comparison of properties.

Colors

The colors produced by the various combinations tried were observed on at least two separate preparations and are described in Table II.

The effect of diluting these solutions was then determined, to note the colors at lower concentrations, and to obtain a measure of the intensity of the colors. The procedure was to measure off from the bottle containing the normal solution (bottle no. 1), 100 c.c. into bottle no. 2, and to add 100 c.c. of distilled water. This process was repeated and the dilution thereby, doubled and redoubled, until a solution was obtained which appeared colorless, when compared with 200 c.c. of pure water in a similar container.

The row of bottles thus obtained showed, in some cases, only a gradual fading out of the original color, but in others, definite changes in color were observed. The attempt has been made to draw up a table which will indicate the nature of the significant changes, as far as is possible to express them in words.

The first column of Table II lists the acids used and their dissociation constants expressed as in the previous table. The second column describes the color of the bottle no. 1 solution containing, if possible, one gram of iron in 250 c.c. of one normal acid. The third column states the colors produced by dilution and a careful study of the words chosen, will show where the gradual and the more abrupt changes occurred. The fourth column gives the final color to be observed and the last column contains the number of the bottle which appears colorless. The concentrations of iron and of acid at all these dilutions could be calculated and recorded, but for this table, the comparisons are made much more striking by merely listing these bottle numbers.

A careful examination of Table II will develop many interesting individual relationships and some points of general importance which may be summarized as follows:

1. The solutions with a red or orange-red color, unless very little iron has been dissolved, retain some color to about the 12th bottle. This corresponds to a concentration of .00043 grams of iron in 250 c.c. (calculated on the basis of an original one gram) and an acid normality of the same value.

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[5] Landolt-Börnstein: "Physikalisch-Chemische Tabellen" (1923).

[6] H. Lunden: "Affinitätsmessungen an schwachen Sauren und Basen" (1908).

TABLE II

Acid K.10^4	Color (no. 1)	Color changes on dilution	Final Color	Colorless Bottle
Formic	intense red			
2.14		2. red		
		3. red orange		
		4. orange		
		5. yellow	pale yellow	12
Acetic	intense red			
.18		2. red		
		3. orange red		
		4. red orange		
		5. orange		
		6. yellow		
			pale yellow	13
Propionic	blood red			
.14		2. red		
		3. red orange		
		4. orange		
		5. orange		
		6. orange yellow		
		7. yellow		
			pale yellow	13
Butyric	orange red			
.15		2. red orange		
		3. orange		
		4. orange		
		5. orange		
		6. pale orange		
		7. pale orange		
		8. pale yellow		
			pale yellow	10
Oxalic	vivid green		pale green	11
380.				
Malonic	green		pale green	6
16.1				
Succinic	orange red			
.66		2. red orange		
		3. orange		
			pale orange	9
Glutaric	red orange			
.47		2. orange		
			pale orange	9

TABLE II (Continued)

Adipic	red orange			
.37		2. orange		
			pale orange	6
Tricarballylic	red orange			
2.2		2. orange		
			pale orange	7
Maleic	orange red			
120.		2. orange yellow		
		3. yellow green		
		4. green		
			pale green	8
Fumaric	colorless			1
10.				
Mesoconic	colorless			1
7.9	(trace of yellow?)			
Chloracetic	red			
15.5		2. orange		
		3. yellow		
		4. green yellow		
		5. green		
			pale green	7
Dichloracetic	green yellow			
500.		2. green	pale green	5
Trichloracetic	very pale			
2000.	green			2
Benzoic	colorless			1
.66				
Phenylacetic	colorless			1
.50				
Phthalic	pale green			
12.6				2
Hydrochloric	green			
	(yellow on standing)			6
Sulfuric	pale yellow green			5

2. The solutions with a green color, all of which easily dissolve a gram of iron, become colorless at about the 6th bottle. This corresponds to a concentration of .03125 grams of iron in 250 c.c. (calculated on the basis of an original one gram) and an acid normality of the same value.

3. There are two combinations, the chloracetate and the maleate, which undergo a very definite change from red to green, merely by dilution.

4. It appears probable that the most important factor in determining the color (and, therefore, the structure) of these complexes, is the strength of the acid involved. The selection of such a large number of acids for these tests was made in order to multiply the evidence in support of this statement.

For the purpose of presenting the results of the color tests in the light of the statement just made, Table III has been prepared by arranging the data given in Table II in a different order. The acids are listed in the order of their dissociation constant values and the relation to the colors is immediately evident. The solutions which contained such small amounts of iron that no colors were seen, might have been omitted, without altering the conclusions reached, but, for the sake of completeness, they have been included.

TABLE III

Acid	$K.10^4$	Color (and on dilution)
Hydrochloric	—	green
Sulfuric	—	pale green
Trichloracetic	2000.	very pale green
Dichloracetic	500.	green yellow—green (2)
Oxalic	380.	vivid green
Maleic	120.	orange red—green (4)
Malonic	16.1	green
Chloracetic	15.5	red—green (5)
Phthalic	12.6	pale green
Fumaric	10.	colorless
Mesoconic	7.9	colorless
Tricarballylic	2.2	red orange—orange
Formic	2.14	intense red—yellow
Succinic	.66	orange red—orange
Benzoic	.66	colorless
Phenylacetic	.50	colorless
Glutaric	.47	red orange—orange
Adipic	.37	red orange—orange
Acetic	.18	intense red—yellow
Butyric	.15	orange red—yellow
Propionic	.14	blood red—yellow

The evidence contained in Table III is entirely in accord with the generalization that the strength of the acid involved is the prime factor in determining the color of the complex formed. One or two very obvious peculiarities of the table, however, must be explained at this point.

It will be observed that oxalic and malonic acids give green colored solutions, even in normal concentrations. Thus, when dichloracetic, maleic and chloracetic acids were selected to check further the generalization, it was supposed that they would act in a similar manner. The appearance of red colors with maleic and chloracetic acids was, therefore, quite unexpected. The color changes on dilution, however, seem to turn these examples into a confirmation of the theory advanced, as the concentration is a real factor in the dissociation of these acids. Thus, the change to green in maleic came at a greater concentration than in chloracetic, while the color in dichloracetic was almost green to begin with, as might be expected.

It seems probable, therefore, that the greens of the oxalate and malonate are not determined solely by acid strengths. As a matter of fact, the oxalate possesses a rather distinctive green color and requires much further dilution than the others before it appears colorless. The evidence obtained with the other di-basic acids seems to indicate, however, that an actual contradiction of the above principle is not involved.

It will be observed that no attempt has been made to explain the significance of the colors produced in these solutions. Thus far, the main objective of this work has been to establish the principle regarding the relations between colors and acid strengths. Before any attempt is made at an explanation, the results of some dialysis, diffusion, electrolysis and other types of experiments should be presented. The evidence obtained in these tests will be described in a subsequent article.

Summary

This study had for its purpose, the collection of more information about the form in which iron exists in organic acid solutions, with particular attention to the possibilities of complex formation and of colloidal properties.

Portions of freshly precipitated ferric hydroxide were dissolved in various organic acids, obtaining concentrations of about one gram of iron in 250 c.c. of one normal acid solutions. Standard methods of analysis were used to determine the exact amount of iron and acid present in each case. The colors of the solutions, the colors on dilution and the relative color intensities were determined for each combination.

The most general conclusion reached was that the most important factor in determining the color of any combination is the strength of the acid involved. It was shown that an arrangement of acids in the order of their dissociation constant values would permit of a definite division into two groups, strong acids with green colored solutions, weak acids with red colored solutions. Further work in support of this generalization will be presented in a later article.

COBALT SULFIDE BANDS IN SOLID SILICA GEL

BY EMIL RAYMOND RIEGEL

When silica gel containing cobalt nitrate is allowed to set, and is then overlaid by a solution of sodium sulfide, black rings of cobalt sulfide are formed in profusion. The first rings are very narrow and very numerous, the later rings become gradually broader, less numerous per unit of length and spaced further apart.

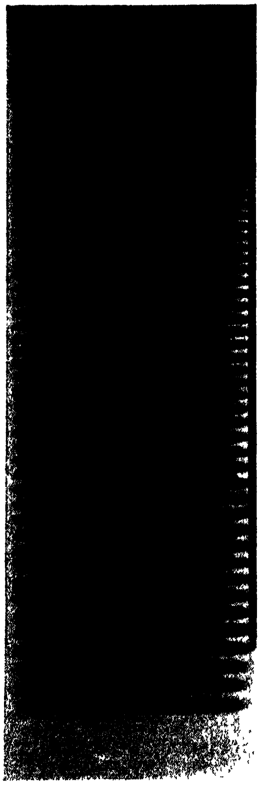

FIG. 1
Cobalt sulfide rings in silica gel. Section of the formation in a flattened pyrex tube

A suitable silica gel is made by pouring 108 cc. of 1.060 commercial sodium silicate solution into 33 cc. water to which 3.5 cc. glacial acetic acid and 0.70 grams cobalt nitrate crystals have been added previously. At once after mixing the two solutions, the resulting mixture, which is still pink, is poured into the special tubes described below, each one receiving 22 cc. The height of the liquid in the tubes is 150 mm from the bottom. The gel sets in about 3 minutes, and is overlaid at once with a 3% sodium sulfide (3% Na_2S) solution. Rings form at once and continue to form over a period of days. A portion of such a tube is shown in the accompanying photograph.

Such was the first procedure. It had the defect of involving a collapse of the upper part of the silica gel, as the solvent action of the alkaline sulfide took place. To measure the rate of advance of the black front, it was necessary to allow for the distance collapsed, which increased from day to day; the first rings were destroyed and so withdrawn from observations; the distance of the top of the gel to any point in the gel changed constantly; there were several other disturbing results so that comparative values over several days were in doubt, the worst one being that the concentration of the sulfide changed in an unknown degree. The first attempt to prevent the collapse was to place the tubes in a nearly horizontal position in a drawer; at the same time any light influence was avoided by keeping the drawer closed. The collapse and solvent action were about the same, however, and the next attempt was to make the sulfide itself into a gel, so as to immobilize the interface. This succeeded. One example follows: 4.5 cc. of 1.060 sodium silicate solution, 0.12 cc. acetic acid, and 1.5 cc. water are well mixed, and 6 cc. of 6% Na_2S solution added and the whole quickly poured on top of the solid cobalt silica gel. Some practice is required to succeed in forming this gel so that it stiffens throughout; it sets so fast that in many cases it was found best to mix the materials in the upper part of the tube itself, which provided a space holding just 12 cc. With this corrected procedure the cobalt silica gel is absolutely undisturbed and its deposits and lines may be observed and measured from a permanent interface days after they are formed. As far as we know, this is the first published example of the growth of Liesegang rings from two gels in contact. In all experiments described below, the tubes were prepared with the sulfide in such a gel, and the tubes were kept in a light tight drawer. The rate of growth of the rings is the same as with the original sulfide solution, if allowance is made for the collapse. The sulfide silica gel is a false gel, but even when partly liquefied, the cobalt silica gel suffers no attack at its upper edge.

Flattened pyrex tubes: The special tubes used were made by sealing off at one end, suitable lengths of a flattened pyrex tubing, supplied in 4′ lengths by the makers. Two sizes were sealed off, one 15 cm long, for preliminary work, the other 22 cm long, the standard length for this work. Its volume, 34 cc., was divided into the lower 22 cc. for the cobalt silica gel, and the upper 12 cc. for the sodium sulfide gel. The advantage of such a tube is twofold: First, the annoying reflection of a round tube, which meets the eye, is avoided, and second, the tube may be laid on the stage of the microscope and examined by reflected and transmitted light at any moment, with no preparation. The inside cross-sectional dimensions of the tubes were 20 by 6 mm with slight variations. All the work described may be successfully performed with round tubes, however.

Modifications studied: The effect on the pattern of various strengths of silica gel (from sodium silicate solution between 1.045 and 1.1000), of the concentration of the cobalt salt (between 0.07 and 0.21 grams crystals in standard tube), and of the concentration of the sodium sulfide, was studied. The pH was observed only casually; in modifying the amount of acetic acid used we were guided mainly by the resulting rate of setting. The more acid the mixture, the slower the set. If the acid is so low that the gel is distinctly blue, it sets before it can be poured into the tubes. The gels used generally were pink, setting in 20 minutes at the longest; or lavender, setting in as little as one minute; blue gels were made by mixing the materials in the tubes themselves. For several cases in which the gel was lavender, the pH was found to be 8.

Two examples of perfect deposition: Two tubes might be described because they illustrate the effect of raising the concentration of the cobalt salt for the same concentration of the silica in the gel, and also because the ring formation was absolutely perfect. The gel was made by pouring 144 cc. of sodium silicate solution into a mixture of 33 cc. water, 3.5 cc. glacial acetic acid and 0.82 grams of cobalt nitrate crystals. One test-tube received 22 cc. of this solution which contained 0.10 grams of cobalt crystals. A second tube was prepared with the same materials in the same proportions except that it contained 1.23 grams of crystals, or to the 22 cc. in the tube, 0.15 grams.

Each gel set in 2 minutes, and was at once overlaid with a weaker silica gel containing 3% Na_2S. The only difference between the two tubes then was the concentration of the cobalt. The daily advance of the outermost black sulfide rings was noted and plotted, giving the two curves adjoined. The higher concentration of cobalt causes a slower advance, confirming several previous results. The sulfide ion may be assumed to enter the two lavender gels at the same rate, but in the stronger (as to cobalt) gel, more sulfide is consumed per unit distance, and there is therefore less left to advance. These two tubes were remarkable in that the rings formed absolutely without fault, none was bent, all were sharp and thin. #1 tube (0.10 grams cobalt salt) gave over a distance of 120 mm a perfect succession of rings, numbering 150. The first ones were 0.1 mm thick, the final ones 1.5 mm in thickness. All the pink color had been drained upward so that near the bottom few rings or deposit of any kind were formed. Number and thickness of rings in #2 were very similar. It will be noted that the curve is not logarithmic, but that the advance is at the same rate from the sixth day to the nineteenth, while it is faster for the first six days. After the sixth day, there is no slackening of the rate of entry for the greater distance which the sulfide ions must cover.

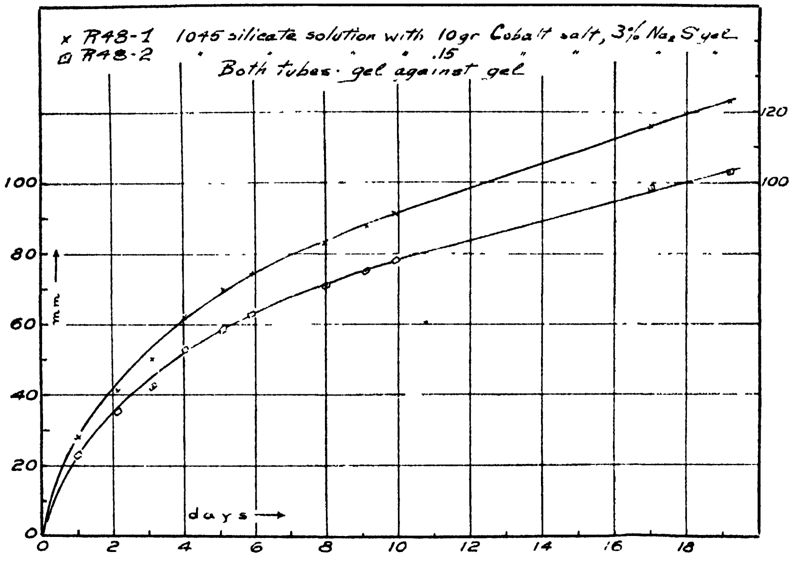

FIG. 2

The concentration of sodium sulfide was varied between 1 and 3%; the greater the concentration of the sulfide, the more rapid the advance.

For different strength of gels, made from solutions of sodium silicate between 1.045 and 1.100 in specific gravity, there was very slight differences. It was hoped that it could be demonstrated that with the more concentrated gels, the advance would be slower, and the lines finer; in general, this was the result, but all tubes did not give this result, so that it must remain in doubt.

The limits in the solution of silicates were chosen as given because solutions weaker than 1.045 gave gels that were not stiff enough, while above 1.100 the resulting gels developed fissures which interfered with the pattern growth.

As to alkalinity, a systematic study was not made; it was indicated however that the blue gels gave more numerous rings, with smaller spacings than gels with lower pH values.

Accompanying phenomena: The matter is not simply an advance of sulfide ions, a meeting with cobalt ions, deposition of cobalt sulfide, draining of the zone below by migration of the cobalt upward onto the sulfide, so that a later advance of the sulfide finds no cobalt for a certain distance, giving rise to the clear space. Several additional observations must be taken into account. (1) The ring is preceded by a brown zone which, with the front halfway down the tube, is commonly 1 mm thick. This might well be molecular cobalt sulfide too low in concentration to reach the solubility product, or colloidal cobalt sulfide not yet coagulated by some other agency. (2) There may be observed in the gels made from 1.060 sodium silicate and stronger, very faint rings barely detectable unless the observer is on his guard. These we have called phantom lines; they are described more fully further on. (3) As the gel sets, its transparency is replaced by a wax-like translucency, very apparent in the pink, lavender or blue gels. (4) Bubbles of air caught in the gel show a surprising behavior, they first grow in size, then decrease, and then completely collapse, leaving a faint trace mark. These bubbles are discussed more fully below. (5) On standing six months or a year, the black color gradually fades out if a slow drying accompanied by shrinkage is provided for. The color returns to a pink, but this gel retains the markings of each ring perfectly, showing that simultaneously with ring formation, a deformation of the gel structure took place.

The phantom rings are not colored, but seems to be merely a more intensely wax-like layer with the thickness of a faint pencil line; they are barely visible in faint reflected light against a dark background, but they are unmistakable. They number 5 to as many as 8, extend beyond the advancing front by 8 or 10 mm, and are to be found only after the front is half-way down the tube; at that stage, the pink color is very pale for these same 8 or 10 mm, and even absent for the first 3 to 4 mm. The weaker gels do not show phantom rings, as indicated in the following table:

of	3	tubes,	from	1.045	sod.	silicate	solution,	0	developed phantom rings
"	10	"	"	1.060	"	"	"	7	" " "
"	3	"	"	1.080	"	"	"	3	" " "
"	2	"	"	1.100	"	"	"	2	" " "

The dark rings form later, one dark ring always resting on a previous phantom line, and growing upward, toward the place of sulfide entry. The phantom rings may be considered due to the distension of a number of interfibrillar cavities whose walls are pressed outward by local events. The relative distribution of fibrils and water is altered so that the proportion of reflected light is greater, hence its visual detection. In a general way this idea is supported by the fact that weak gels do not possess them, while strong gels do. In the weak gel the proportion of wall substance is too small so that doubling it, let us say, should cause a visible alteration; in the stronger gel the distended walls carry with them nearby fibrils so that the aggregate is distinctly different from the average structure. Each phantom ring becomes the base of a black ring subsequently formed; no black rings form between the phanthom rings.

Bubbles in the gel: The history of some of these might be given to indicate the pertinence of the observation. In one tube (R-42-3), made from 1.060 silicate solution, containing .21 grams cobalt crystals in 22 cc., overlaid with 3% Na_2S gel, the cobalt-silica gel solution was poured in rather late, after it had become lumpy. It was hoped that the lumps would coalesce, giving the usual homogeneous gel, in which therefore the rings would grow with regularity. But on looking through it, the gel showed striae and cords; it was not homogeneous. Moreover, it contained a great many bubbles. It turned out that the rings formed with fairly regular shapes, much more so than expected.

After the front had advanced 26 mm, it was noticed that the next 6 mm were free from bubbles, whereas just before, it had contained many. The next day, the front had advanced to 35.5 mm and the region between 35.5 and 42 mm was now cleared of bubbles. From 42 on, the bubbles were numerous, thus between 42 and 47 mm 100 bubbles were counted. The next day, these were gone, while the front was at 40. The region cleared of bubbles gradually grew from 6.5 to 12, then to 14 mm, ahead of the front. It is clear that in this paler pink zone, some change other than cobalt sulfide formation was taking place in the gel: water from the upper more hydrous gel, entered in addition to the sulfide ions, swelling the gel, closing and obliterating the bubbles. The air these contained disappeared partly through chemical reaction, partly by solution under pressure. A gel made with sodium silicate of 1.100 specific gravity has such a great tendency to contract that the gel parts, and fissures form, after one or two days, within the tightly closed container. Hence if it is the normal tendency for the silica gel to contract, because for example the fibrils take up water of hydration and change it to water of constitution, it must be that the bubbles are squashed because new waters enters the neighbourhood, swelling the gel, overcoming the contracting tendency completely and reversing it, so that it becomes a swelling.

That the gel contracts is shown besides by the change in the surface of the portions poured into the flat tubes. It is at first nearly flat; after two days it becomes a deep dish (7 mm deep), with the tube closed to prevent evaporation.

The events for single bubbles of air caught in the gel were followed on the microscope:

Two bubbles in the same tube:

Measured by square-ruled micrometer, side of small square = .0814 mm.

	Large bubble	Small bubble
10.00 AM	5.5. by 5 squares	$2\frac{1}{3}$ by $2\frac{1}{3}$ squares
10.28	$6\frac{1}{2}$ by 4.8 " ; it had grown	$2\frac{1}{2}$ by $2\frac{1}{2}$ sq.; larger
10.49	7 by 5 " ; still growing	
12 noon	6 2/3 by 5 sq.; it had stopped growing	
2 PM	5.4 by 4.6 sq.; now shrinking	$2\frac{1}{2}$ by $2\frac{1}{2}$
4.45	$4\frac{1}{2}$ by $4\frac{1}{2}$	2 by 2
7 PM		1.7 by 1.7
9 PM	$4\frac{1}{2}$ by 4	.6 by .6
Next morning	gone	gone

The history of numerous other single bubbles was recorded; in all cases it agreed with that of the two noted above. The growth is due to the contraction of the gel; the shrinking is due to entering water.

It seemed likely that an explanation of the growth of the rings might be offered on the basis of sacks which are distended, with walls consisting of fibrils, coated in and out with cobalt sulfide. Before stating it more fully, an additional set of observations will be recorded.

Cobalt sulfide bands on a microscope slide: The cobalt sulfide bands in silica gel can also be grown in a thin, flat layer of the gel mix, so that all deposit dots may be observed. On a large section of thin glass a few drops of the cobalt-silicate mix are placed and immediately covered with a 20 by 20 mm cover glass which is pressed down firmly to force all but a thin layer of liquid out. The excess liquid is removed with filter paper. A dam of plastic clay is placed all around the edges of the large slide. By that time, the gel has set and a water solution of 3% Na_2S is placed around the cover glass, taking care to keep the top of the cover glass free. The deposit forms at once and is followed under the microscope, using direct light from the mirror below the stage. Bands form as fast as the sulfide enters and their genesis, growth and possible further change are followed with the low-power objective (10x) and a 17x eye piece in which a square ruled micrometer has been slipped. The duration of the experiment till the center of the cover glass has been reached from all directions is 60 minutes. Some of the details are best shown by an example:

11.56 AM	start
12 5 PM	7 fine lines (ripples) are plainly seen; growth at the rate of 1 a minute
12 10	14 bands are formed
12 19 30	watched special group of lines; sixth beginning
12 21 30	sixth and seventh finished

The time for one band or ripple to form from first faint appearance to completion is 1 minute. Such a band is shown in figure 3, with a portion of the two adjacent bands. After the previous band is finished a darkish area becomes perceptible a little distance from black edge of the previous line. The dark area deepens, begins to show detail; then the far edge sharpens like a black border being drawn. The next band appears as a faint gray area gradually growing; when the eye returns to the previous band, as quickly as possible, it is finished, not to be altered by standing. It consists of numerous dots, smaller on the sulfide entry slide, and fewer dots about 5 times larger, on the far side, as shown in the micrograph.

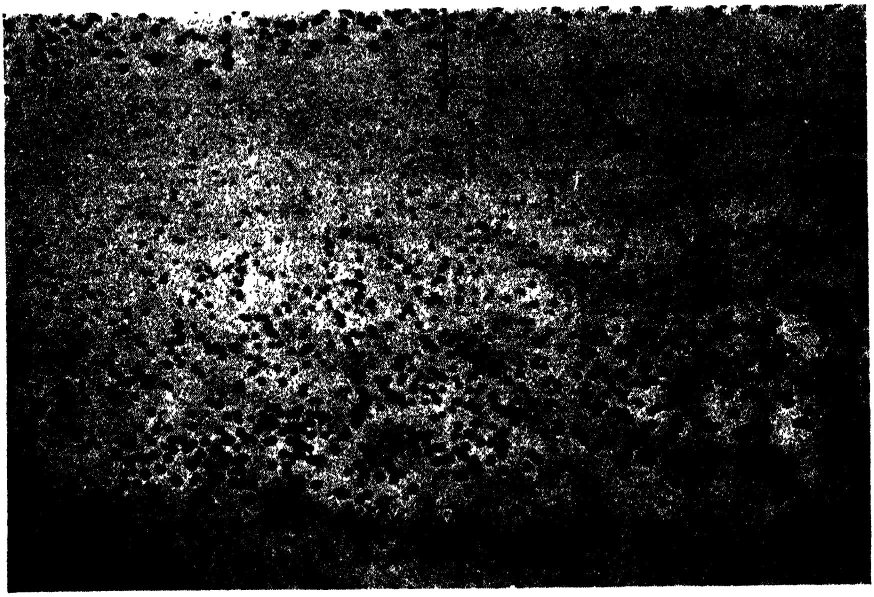

Fig. 3

Cobalt sulfide band in silica gel on a microscope slide; magnification 180 diameters. Direction of entry of sulfide shown by arrow.

The several events are explained as follows. The periodicity in the concentration of cobalt ions is the usual one. As the entering sulfide ions pass beyond the large dots of the previous band, which drain the area behind them of some of its cobalt, there are fewer cobalt ions at first. The dots which form are numerous but small. Cobalt ions drain in at a rapid rate, but arrive in time only to form, or assist in forming the rear dots. A wave of water now follows, as it reaches the nearer fine dots, these have set so hard that their walls are no longer permeable, but the water reaches the rear dots while they are still in the act of forming. Their walls are still plastic and permeable to water. The concentration of all ions in the mass of the gel is so lowered that water is drawn into the spheroidal dots, by virtue of the momentarily higher concentration within the sack. The cobalt exhausted locally, the sulfide ions pass on, while water is still being drawn into the sacks. After the first small dots of the next band are formed, the events are repeated in the same order.

Following the conception of gel structure of Arsem[1] this gel may be considered as consisting of the associated phase, the silica, arranged in an imperfect lattice, with rather large voids ("segregated gel") as compared with molecular dimensions, filled with the free phase, water. The silica is hydrated. At first, cobalt ions are distributed uniformly throughout the free phase. As the sulfide ion enters, it binds the cobalt as molecular cobalt sulfide. The concentration of ions, now lowered, allows rapid diffusion from below (the pink region) and in part, from the same level, into the chamber or sack. The work of wall building now begins. The black sulfide attaches itself to the wall, enlarging its fibrils until the wall is continuous, still highly hydrated, and soft and plastic. A wave of water lowers the concentration outside the chamber. Water is sucked in by osmotic suction, the soft walls distending, assuming a more nearly spherical shape, growing in fibril material as the walls reach the fibrils of other chambers, which failed to develop into sacks. Cobalt ions left in the free phase diffuse to the wall of the sack, there to meet sulfide ions and react to form black sulfide which enmeshes itself into the wall fibrils. Any molecular cobalt sulfide formed also reaches such walls, except perhaps an amount not detected by the microscope. The chambers are unequal; that every chamber in the lattice does not become a dot is due to the advantage which the larger size gives. The larger chambers contain more cobalt ions, and later more black sulfide per unit of wall, than the smaller chambers; later when adsorption from the outside takes place the larger sacks again have the advantage, for a greater surface is offered. The number of dots and the distance between them is a function of the distance the ions concerned migrate under the impulse of low concentration zones, and of the degree of inequalities between the chambers. In this case the distance is from 2 to 10 times the diameter of the larger dots.

Periodicity of water entry: The study of line formation on the slides has the advantage that once deposited, there is no further change. The events take place rapidly. The layer of gel mix is so thin that all the dots formed are visible and in focus. The formation of small dots on the sulfide entry side, and large dots on the far side, is well explained by the assumption that water from the outside solution enters the gel, and that this entry is periodic. That water enters the gel is established by the obliteration of the bubbles in the large flat tubes; it is reasonable to assume therefore that in the case of the band formation on the slide, there is also a water entry.

Other supporting factors: In the tall, flat pyrex tubes used, a content of 0.07 grams of cobalt nitrate crystals in the 22 cc. of cobaltic gel is not sufficient to give rings down to the bottom, a quantity of 0.10 grams is. Hence in such a tube with 0.10 grams of $Co(NO_3)_2.6H_2O$ can develop a maximum of 0.0313 grams CoS. For the 150 rings formed, requiring all the cobalt in the gel, there is available for each ring 0.00027 grams CoS. Each ring consists of numerous dots, as shown in the micrograph, Fig. 4. The average number of dots per ring is 500 at least, so that for each dot 0.0000006 grams must suffice. The content of silica in the space occupied by a ring is 30 times greater. It is evident that the dots do not consist of cobalt sulfide, but rather of hydrated silica, tinted with a small amount of the black sulfide. This conclusion is strengthened by still another observation briefly stated above, but repeated more fully here. When the tubes are allowed to stand loosely stoppered for a year, the black color gradually fades out, and the pink color returns. The sulfide is oxidised by the air to the sulfate. The pink gel however retains the markings of each ring, not to be altered until the gel crumbles through loss of moisture. In the formation of the rings, an alteration in the gel structure essentially as suggested, has taken place.

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[1] William C. Arsem: Gel Structure, J. Phys. Chem., **30**, 306 (1926).

Therefore the phantom rings, the changes indicated by the bubbles, the rapidity of formation of the dots in graded sizes on the slides, the small weight of sulfide available per ring, the markings in the residual faded-out gels, all fit the theory of sack formation and distension by periodically entering water, with the resulting dots consisting essentially of silica tinted black by a small amount of sulfide.

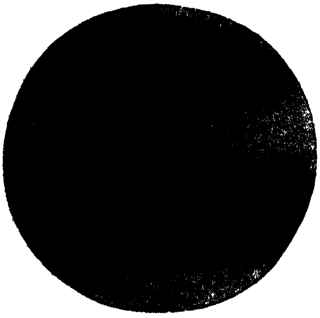

Fig. 4
Cobalt sulfide ring in the pyrex tube; × 40

Analysis: The sodium silicate used was a commercial syrup with a silicate composition expressed by $Na_2O+3.40\ SiO_2$, therefore fitting the table in the handbooks labelled $Na_2O+3.36\ SiO_2$. All the solutions were taken from this single batch.

Previous work: A valuable paper has appeared describing numerous periodic stratifications of cobalt sulfide in solid gelatine gel, produced by ammonium sulfide, the entering agent, in gelatine containing cobalt-sodium nitrate.[2] As far as could be found, cobalt sulfide bands in silica gel have not been reported before.

Acknowledgments: Preliminary experiments which established the possibility of forming cobalt sulfide bands in silica gel were performed by Mr. Leo Widgoff, A.M. in 1926, in this laboratory. The method used in forming the bands on the microscope slide was devised in the course of other experiments by Mr. Melvin C. Reinhard, A.M., also in this laboratory.

Summary

Cobalt sulfide bands may be developed in solid silica gel, by overlaying the solid gel containing cobalt nitrate with sodium sulfide solution, or preferably a second silica gel, more hydrous, containing sodium sulfide. An instance is thus furnished of rhythmic bands developing from two gels in contact.

Flat pyrex tubes are described which facilitate observation on the low power microscope.

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[2] F. E. Lloyd and V. Moravek: Plant Physiology, 3, 101-30 (1928).

The behaviour of air bubbles in a gel in which Liesegang band are in process of forming is reported.

Cobalt sulfide bands on a microscope slide have been studied, an explanation is offered for the rapid formation of band formation and for the details in its structure, primarily fitting the bands grown on such slide. The same explanation may be used for the bands on the larger scale of the pyrex tubes. Essentially it presents a mechanism accounting to the visible deformation of the silica gel locally, a periodic entry of water following the periodic play of cobalt ion concentration is assumed. In the large tubes, there is in addition an entry of water before the formation of the black bands; it is this early water which destroys the bubbles.

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THE PREPARATION AND TESTING OF NICKEL CATALYSTS FOR HYDROGENATION*

BY HOMER ADKINS AND LLOYD W. COVERT

In the course of an investigation of the hydrogenation of organic compounds over nickel and other base metal catalysts it seemed desirable to compare the relative merits of different catalysts. It was then necessary to consider what characteristics of the catalyst should be used as a basis for comparison. A catalyst for hydrogenation may have merit in a number of different ways, for example, catalyst X may be better than catalyst Y in that (1) it is possible to hydrogenate at a lower temperature or (2), pressure than with catalyst Y; or (3), less of X than of Y may be required to give a certain effect; or (4), catalyst X may cause a more rapid rate of absorption of hydrogen under a given set of conditions than does catalyst Y; or (5), a given amount of X may cause complete hydrogenation of a given weight of material in less time than does the same amount of Y; or (6) less of some undesired reaction may occur with X than with Y.

The more important variables that determine the numerical values which may be assigned to these characteristics are even more numerous than the characteristics which they modify. The rate of hydrogenation over a nickel catalyst may vary with (1) the acceptor of hydrogen, (2) the impurities in the latter, (3) the temperature during hydrogenation, (4) the pressure of hydrogen, (5) the amount and (6) kind of solvent, (7) the amount of catalyst, (8) the ratio of catalyst to hydrogen acceptor, (9) the time and (10) the temperature involved in all stages of the hydrogenation experiment, (11) the thoroughness of the mixing of the hydrogen acceptor, catalyst, and hydrogen. The last of these factors is made up of at least two components, one of these being the rate or thoroughness of mechanical agitation of the reactants, and the other the ease of dispersion of the catalyst in the reaction medium.

It will appear that not only the *numerical* but also the *relative* values of the characteristics of the various catalysts are dependent upon the acceptor of hydrogen, temperature, pressure, and the other variables referred to above, which are actually used in the testing of the catalysts. It is one of the primary purposes of this paper to exhibit experimental evidence that general and sound conclusions as to the relative activities of nickel catalysts, for example, may not be reached as the result of following what may be termed a conventional method of scientific work. By this is meant the method in which each factor is in turn varied while the other factors are held constant, followed by the tacit assumption that if there are for example three variables X, Y, and Z, the effect of varying X and Y *simultaneously* may be concluded from a knowledge of the effect of varying X and Y separately.

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*A Communication from the Laboratory of Organic Chemistry of the University of Wisconsin.

For example, it will be shown that the relative merits of two catalysts are not the same for two different acceptors of hydrogen, nor for different characteristics of the catalyst, and therefore, it may be suspected that even the relative merits are not independent of the other variables, such as temperature, ratio of catalyst to acceptor, etc. which have been listed above. It has been shown in a previous paper[1] that the effect of variation in the pressure of hydrogen was rather specific for the compound undergoing hydrogenation, and it may be suspected that it differs with other variables such as the catalyst.

One may well be appalled at the amount of work involved in acquiring sufficient data to justify drawing positive conclusions on a reaction which involves six or more measurable characteristics and perhaps twice as many variables. This is especially true if the effect of simultaneous variability may not be predicted from a knowledge of the effect of the variation of one factor at a time. It is not the intention of the authors to attempt any such systematic survey but rather in the future to give especial consideration to those factors which determine the ratio of competitive or simultaneous reactions over nickel catalysts.

Preparation and Method of Treating Catalysts

In the experimental work described in this paper numerical values have been assigned to four of the characteristics of eight nickel catalysts for the hydrogenation of acetone, resorcinol, toluene, and benzyl alcohol. The temperature and the amount and ratio of catalyst to acceptor used for the hydrogenations were chosen because they gave a reasonably rapid rate of hydrogenation. The pressure of hydrogen (100 atmospheres) used is quite effective and is one that may be used without expensive equipment.[1] The rate of shaking of the reactants (41 cycles per minute) was one that has appeared to give a good suspension of the catalysts. The units for heating the bomb were of such a capacity that the contents of the bomb could be heated to 125° in 30 minutes and to 175° in 55 minutes.

Resorcinol, benzyl alcohol and acetone were hydrogenated at 125° while with toluene the temperature regulator was set for 175° but due to the rapidity of the hydrogenation the temperature of the toluene in some cases rose to about 250°. Two g. of catalyst containing approximately 16 percent of nickel was used with 1 mole of acetone, 0.62 moles of resorcinol and 0.23 moles of benzyl alcohol. Three g. of catalyst was used with 0.935 moles of toluene. Thirty five ml. of anhydrous ether was used as a solvent in the hydrogenation of resorcinol.

Seven different methods for the preparation of nickel catalysts were used in this investigation. Three of these involved differences in the source of nickel. In two of these the nickel was from nickel nitrate of varying purity and in one was from nickel chloride. Three different reagents, i.e., sodium carbonate, sodium bicarbonate, and potassium hydroxide were used for the precipitation of nickel on the kieselguhr support. Two different methods for mixing the reagents were used. One of these (Method A) involved the addition of the soluble nickel compound (on kieselguhr) to the precipitant, in the other (Method B) the reverse order was followed, i.e., the addition of the precipitant to the soluble nickel compound (on kieselguhr).

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[1] Adkins, Cramer, and Connor: J. Am. Chem. Soc., **53**, 1402 (1931.).

In the preparation of all catalysts the solution of the nickel salt was thoroughly incorporated into the kieselguhr by grinding the partly moistened powder in a mortar until it was of a cream-like consistency. This procedure which was originally suggested and used by Mr. Karl Folkers in this Laboratory, makes it possible to easily reproduce very active catalysts. The use of kieselguhr as a support for a nickel catalyst has been criticised because difficulty was experienced in reproducing the activity of catalysts. A similar difficulty was encountered in this Laboratory until Folkers' procedure was used. All catalysts were washed as previously described[1] except that they were suspended twice instead of once in 300 ml. of water. The concentration of the various precipitating solutions used with 100 g. of acid washed kieselguhr and 100 g. nickelous nitrate hexahydrate (or its equivalent) in 150 ml. of water were as follows:—120 g of sodium carbonate decahydrate in 100 ml. of water, 60 g. sodium bicarbonate in 260 ml. of water, 24 g. of potassium hydroxide in 100 ml. of water. Sodium bicarbonate as a precipitant was first used in this Laboratory by Mr. Ralph Connor who did so on the supposition that a basic nickel carbonate of more uniform composition could be obtained under certain conditions with this reagent than through the use of sodium carbonate.[2] The methods and reagents used in preparing each catalyst are indicated in Table I.

Reagents:—A "C.P." grade of nickel nitrate from the Baker and Adamson Company was used unless otherwise noted. Nickel nitrate prepared from the reaction of "C.P." grade nitric acid and pure nickel pellets from the International Nickel Company was used in the preparation of catalyst 11 Cv. The toluene b.p. 110.5-111° was C.P. grade free of sulfur. The acetone had a b.p. of 56.5 while the resorcinol was a U.S.P. grade m.p. 110°. The best grade of benzyl alcohol from the Eastman Kodak Company was further purified since rather erratic results were obtained in attempting to reduce different lots of this product. The alcohol was refluxed 12 hours with a 35 percent solution of potassium hydroxide, and then distilled through a Widmer column at 203.5-205.0°. The product was then heated for 5 hours at 100°, under 70 atmospheres of hydrogen with reduced nickel. This removed any halogen containing impurities. The nickel was prepared by the reduction of 5 g. of nickel oxide (prepared by the decomposition at 250° of nickel carbonate) for four hours at 350°. The amount of nickel so obtained was used with 150 ml of alcohol.

The products from the hydrogenation of benzyl alcohol were fractionated, toluene being collected 108-112° (740 mm) and cyclohexyl carbinol 175-185 (740 mm) by far the greater part coming over 179-180°. Cyclohexanol and cyclohexanediol 1-3 from the hydrogenation of resorcinol were collected at 60-65° (10 mm) and 124-134 (10 mm) respectively, although in most cases at least 90 percent distilled over a 1° range. The products from the hydrogenation of toluene and acetone were methyl cyclohexane and propanol-2, respectively, and each distilled over a 1° range.

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[1] Adkins and Cramer: J. Am. Chem. Soc., 52, 4351 (1930).

[2] Cf. Gmelin-Kraut: 5, 108.

The kieselguhr used as a support for the nickel catalyst was in most cases from the Meyer Drug Company, St. Louis. However, there appeared to be no difference in activity between the catalysts on this support and those on "Filter-Cell" supplied by the Johns-Manville Company, New York.

The apparatus and method of experimentation were essentially the same as those previously described by Adkins and Cramer.

Reproducibility of Results:—The extent of variation in the data obtained in different experiments with duplicate samples of catalysts and with samples of catalysts prepared in the same way but at different times is indicated by plus and minus figures given in Tables I and II. All significant experiments were duplicated at least twice while the total number of hydrogenation experiments on which this paper is based is 145.

Comparison of Catalysts

The relative merits of catalysts may be compared in a number of different ways as noted above. Four of the characteristics of nickel catalysts will be considered in this comparison. The experimental basis for the first comparison is the time required for the adsorption of the middle 60 percent of the total amount of hydrogen absorbed. For this purpose the time for the absorption of the first and last 20 percent of hydrogen is disregarded. This comparison is thus between the activities of catalysts during the chief period of activity.

There is tabulated in Table I the time for the 60 percent of hydrogenation used as the basis for the first comparison. Limiting the comparison for the moment to the four catalysts made by the two methods through the use of sodium carbonate and sodium bicarbonate, it may be seen from the data in the table that they are all four quite active towards toluene, the differences between them being small. For acetone the bicarbonate A method catalyst (10 Cv) was distinctly inferior to the other three catalysts. The carbonate A method catalyst (8 Cv) was distinctly inferior as regards the rate of hydrogenation of benzyl alcohol and of resorcinol. The B method of preparing catalysts is better than the A method in every case for the carbonate catalysts (15 Cv) and is better than or as good as the A method in case of the bicarbonate catalysts. However, with no compound is the difference between the two methods as marked with the bicarbonate as with the carbonate catalysts.

Extending the comparisons to include the eight catalysts it may be said that potassium hydroxide may be used as a precipitant for nickel, the resulting catalyst (13 Cv) being somewhat inferior to the corresponding carbonate catalyst except for benzyl alcohol. A similar statement may be made in

TABLE I

Time in Minutes for Hydrogenations over Various Catalysts[1]

Catalyst	Toluene	Acetone	Benzyl Alcohol	Resorcinol
8 Cv ($Ni(NO_3)_2 + Na_2CO_3$) A	7.5 ±1.5 (11)	12.5 ±3 (27)	15 ±2	430 ±75 (1250)
15 Cv ($Ni(NO_3)_2 + Na_2CO_3$) B	6.5 ±2.0 (26)	11.5 ±2 (18)	8 ±1	275 (490)
10 Cv ($Ni(NO_3)_2 + NaHCO_3$) A	8.7 ±0.7 (21)	18.5 ±2 (56)	8.5 ±0.5	260 ±25 (540)
16 Cv ($Ni(NO_3)_2 + NaHCO_3$) B	6 ±1.0 (14)	13.7 ±2 (34)	8 ±2	217 ±8 (490)
13 Cv ($Ni(NO_3)_2 + KOH$) A	9.7 ±0.8 (24)	16 ±1 (37)	7 ±1	350 ±13 (900)
12 Cv ($NiCl_2 + NaHCO_3$) B	7.5 ±1.0 (20)	13.8 ±1 (30)	4.5 ±0	220 ±50 (425)
11 Cv ($Ni(NO_3)_2 + Na_2CO_3$) A	8 ±2.0 (17)	16 ±4 (31)	12 ±3	265 ±65 (715)
13 HC ($Ni(NO_3)_2 + Na_2CO_3$) A	36 ±18 (60)	40 ±10 (66)	19 ±2	562 ±12 (1410)

[1] The figures in parenthesis are the average times for complete hydrogenation, while the others are for the "middle 60 percent" of hydrogenation.

regard to nickel chloride as a source of nickel except that toward benzyl alcohol and resorcinol it was one of the most active catalysts used in this investigation.

The catalyst (11 Cv) prepared from nickel nitrate made in this Laboratory from C.P. nitric acid and C.P. nickel pellets was not much more active than that made from the Baker and Adamson nickel nitrate. The catalyst prepared by Cramer (13 HC), which was one of the most active of those used in his experimentation, was very distinctly inferior to the catalyst prepared by the modified method described in this paper.

The experimental basis for a second comparison of catalysts is the temperature at which the pressure of hydrogen reached a maximum and will be referred to as the "inflection temperature". This temperature is the one at which the rise in the pressure of hydrogen due to the rise in temperature of the bomb was compensated for by the absorption of hydrogen. Along with this may be considered the percentage of the compound which was hydrogenated before the temperature set for hydrogenation was reached. These two experimental observations in almost all cases parallel each other and both give an insight into the behavior of the catalyst in its youth. For toluene the inflection temperature was approximately 105° for 15 Cv, 10 Cv, and 16 Cv while for 8 Cv it was 130°. For acetone the inflection temperature was 80° for 15 Cv and above 100° for the other catalysts. For benzyl alcohol catalyst 12 Cv gave an inflection temperature of 90° while for the others the inflection was well above 100°. Only 15 Cv, 10 Cv, and 12 Cv gave inflection temperature, with resorcinol. In the case of 15 Cv with acetone 53 percent was hydrogenated below 125° while with other catalysts the amount so hydrogenated was usually less than 30 percent. With benzyl alcohol 83 percent of the compound was hydrogenated below 125° with catalyst 12 Cv while with most of the other good catalysts only 50 to 60 percent so reduced.

The experimental basis for the third comparison is the time required for the absorption of all the hydrogen. These values are given in parenthesis in Table I. Toluene is hydrogenated so rapidly and the reaction is so exothermic that the hydrogenations did not occur under identical temperatures. However, it should be noted that catalyst 8 Cv which was quite inactive at low temperatures gave a complete hydrogenation in the shortest time (11 minutes) as compared with the bicarbonate catalyst 10 Cv which required 21 minutes and 13 HC which required 60 minutes. With acetone the bicarbonate catalysts (10 and 16 Cv) required a distinctly longer time (34 to 56 minutes) than did the carbonate catalysts (8 and 15 Cv) (18 to 27 minutes). With resorcinol catalyst 8 Cv required 1250 minutes while 15, 10, and 16 Cv need approximately 500 minutes.

The fourth basis of comparison is only applicable to benzyl alcohol and resorcinol for it involves the ratio of products formed, i.e., toluene and cyclohexyl carbinol from the former and cyclohexanol and cyclohexanediol 1-3 from the latter compound. There is recorded in Table II the percentage yield of these products over six catalysts. Only the two products mentioned above are formed from benzyl alcohol, so that the percentages of toluene and cyclohexyl carbinol add up to 100 percent. However, in the case of resorcinol there is formed over some catalysts (notably 8, 13, and 15 Cv) considerable quantities of condensation products so that the percentages of cyclohexanol and cyclohexanediol add to 78, 87, 84, 94, and 100 percent for the various catalysts.

The carbonate catalysts gave 150 to 200 percent as much cyclohexyl carbinol as did the bicarbonate catalysts. The potassium hydroxide catalyst gave the lowest yield of the alcohol. The bicarbonate catalysts gave the better yields of cyclohexanediol 1-3 from resorcinol, the B method of catalyst preparation being very much superior. The A method with the carbonate gave the same yield of cyclohexanol as did the B method with the bicarbonate. If A and B are interchanged in the above sentence it is still true. It is rather striking that the catalyst (16 Cv) which was least active in eliminating a hydroxyl from resorcinol was the most active (of the carbonate and bicarbonate catalysts) for the removal of the hydroxyl group in benzyl alcohol.

TABLE II

Proportion of Products from Hydrogenation of Benzyl Alcohol and Resorcinol over Various Nickel Catalysts

Catalyst	Benzyl Alcohol		Resorcinol	
	Toluene	Cyclohexyl Carbinol	Cyclohexanol	Cyclohexanediol 1-3
8 Cv (Na_2CO_3) A	73 ±3	27 ±3	11 ±2	67 ±3
15 Cv (Na_2CO_3) B	70 ±1	30 ±1	22 ±1	65 ±2
13 Cv (KOH) A	90 ±2	10 ±2	16 ±1	68 ±1
10 Cv ($NaHCO_3$) A	82 ±2	18 ±2	20 ±1	74 ±1
16 Cv ($NaHCO_3$) B	85 ±2	15 ±2	11 ±1	89 ±1
13 HC (Na_2CO_3) A	66 ±2	34 ±2	8 ±1	75 ±3

It thus appears that the factors which determine the activity of a catalyst for the absorption by a hydrogen acceptor are quite different from those which determine the relative rates of what must be simultaneous and competitive reactions. For example, catalysts 15 Cv and 16 Cv gave very similar rates of hydrogenations for resorcinol while with 15 Cv the ratio of cyclohexanol to cyclohexanediol was 1 to 3 while with 16 Cv it was 1 to 8 or more. Catalyst 8 Cv and 13 HC were similar to 16 Cv in ratio (1 to 6 and 1 to 9 as compared with 1 to 8) yet the two latter catalysts were very inactive as compared to 16 Cv.

Catalysts not made by Precipitation:—The above comparison of catalysts was confined to the type in which a nickel compound was precipitated on kieselguhr, because it has seemed to us that this type of nickel catalyst was quite superior to those obtained by decomposing nickel nitrate or nickel carbonate either alone or on a support. Brown, Etzel, and Henke[1] among others decomposed nickel nitrate on kieselguhr and reduced the resulting oxide for several hours, and Bradt[2] reduced nickel carbonate. The following experimental evidence may be cited in justification of our preference for the "precipitated on kieselguhr" type of catalyst. Bradt obtained a 100 percent hydrogenation of p-nitrophenol within 120 minutes or less using a ratio of 1 part of nickel carbonate to 5 parts of p-nitrophenol at 125°, and 34 atmospheres pressure. A catalyst prepared in this Laboratory according to his directions brought about the complete hydrogenation of p-nitrophenol in 75 minutes. One part of our catalyst 16 Cv to 17 parts of p-nitrophenol induced 100 percent hydrogenation within 25 minutes, 90 percent of the hydrogenation occurring within 10 minutes. If the ratio of nickel to nitrophenol had been as great in this case as in the experiments of Bradt the nitro group would no doubt have been completely hydrogenated within a very few minutes. Catalyst 16 Cv brought about the complete hydrogenation of toluene and acetone in 14 and 34 minutes respectively while under identical conditions the catalyst prepared by Bradt's method did not give complete hydrogenation after 5 hours. Nickel catalysts prepared by reducing nickel oxide, deposited by decomposing nickel nitrate on kieselguhr as by Brown, Etzel and Henke, were very much inferior even to those prepared by Bradt's method. It should be pointed out that almost any nickel catalyst will bring about the hydrogenation of easily reducible substances such as acetone and sulfur-free nitro compounds but that the hydrogenation of toluene and resorcinol impose a more severe test upon a catalyst.

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[1] Brown, Etzel, and Henke: J. Phys. Chem., **32**, 633 (1928).

[2] Bradt: J. Phys. Chem., **34**, 2711 (1930).

Summary

Various bases for the comparison of nickel catalysts have been suggested and experimental evidence has been given that the relative merits of catalysts may vary with the basis of comparison, as well as with the particular compound and experimental conditions under which the comparisons are made. In particular it has been shown that for nickel catalysts there is no necessary relationship between the rate of hydrogenation and the relative rates of competitive hydrogenations. Improvements in the methods for the preparation of nickel catalysts have been described and the relative values of different precipitants for depositing nickel compounds on a carrier have been measured for the rate of hydrogenation of toluene, acetone, benzyl alcohol and resorcinol. The ratio of cyclohexyl carbinol to toluene and of cyclohexanediol 1-3 to cyclohexanol produced from benzyl alcohol and resorcinol respectively has been determined for the catalysts described.

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THE DETERMINATION OF SORPTION ISOTHERMALS ON CHARCOAL BY THE RETENTIVITY TECHNIQUE—EXPERIMENTS WITH CARBON TETRACHLORIDE AND WATER

BY A. J. ALLMAND AND L. J. BURRAGE

A new technique for the determination of the sorption isothermals of vapours on charcoals—the retentivity method—has recently been described.[1] It was stated that the isothermals obtained by this method showed discontinuities, being made up, in fact, of a series of loops cutting one another at definite pressures. The present paper contains details of the results obtained, and deals, in particular, with the evidence for the discontinuous structure mentioned.

The majority of the charcoals have already been described, viz. A,[2] B,[2] C,[2] G,[3] H,[3] K,[1] L.[1] The new charcoals M2, M3, and M4 are all steam activated, and made from the same raw material (palm nut kernel). They form a series of decreasing bulk density (determined on particles of 10-12 mesh, respectively 0.584, 0.478 and 0.477), to which corresponds an increasingly severe treatment during activation. M1 (bulk density 0.62) is an unactivated charcoal prepared from the same raw material by simple carbonisation, without subsequent steam treatment.

Table I contains a synopsis of certain relevant facts concerning the experimental work and the results. Column 1 gives the designation of the charcoal, column 2 the number of separate charcoal containers making up the total composite charcoal column, column 3 the initial pressure (in mm.) of vapour at which the charcoal was saturated, column 4 the number of points on the experimental retentivity curve, *i.e.* the number of times during the experiment that the air-stream was stopped and the charcoal containers weighed, column 5 the number of tangents drawn to the derived retentivity curve obtained by logarithmic extrapolation, and column 6 the number of breaks found in the derived isothermal.

Figs. 1-4 contain in detail examples of the actual isothermals obtained.

In Table II are collected the pressures in mm. at which the *three lowest breaks* have been found with different carbon tetrachloride isothermals. To these data are added the corresponding figures for the three most satisfactory experiments carried out with water vapour, *viz.* those with Charcoals G, K (after thorough previous extraction with water in order to remove hygroscopic mineral matter[4]) and M4. It will be noticed that Charcoal G gave an additional break on its water vapour isothermal at a lower pressure, 0.07 mm.,

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[1] Burrage: J. Phys. Chem., **34**, 2202 (1930).

[2] J. Phys. Chem., **32**, 452 (1928).

[3] J. Soc. Chem. Ind., **47**, 372 T (1928).

[4] See Allmand and King: Proc. Roy. Soc., **130A**, 210 (1930).

TABLE I

Nature of isothermals	1	2	3	4	5	6	Remarks
Water Vapour 25°C.	B	3	16.0	12	61	26	Very uncertain below 3 mm.
	A	4	16.0	8	41	12	Results of doubtful accuracy.
	do.	3	18.6	12	62	17	Not taken below 5 mm.
	C	4	12.8	30	65	16	Experimental work not accurate enough to justify the drawing of more tangents.
	M1	2	12.8	14	72	9	
	M2	2	12.8	10	62	12	
	M3	2	15.5	12	74	25	Accurate down to 5 mm.
	M4	2	18.6	16	167	38	The two most accurate experiments with water vapour.
	G	3	18.6	25	155	41	
	K	3	12.8	18	68	13	Early work—not very accurate.
	K (water extracted)	3	15.5	17	102	35	An accurate experiment.
	L	6	12.8	10	119	19	Early experiments. Not sufficiently accurate for more tangents.
	H	3	15.5	15	106	19	
Carbon tetrachloride vapour. 100°C.	B	3	33.0	7	183	29	Accurate below 15 mm. The two series gave practically the same extrapolation.
	do.	3	do.	11			
	B (acid extracted)	3	do.	12	115	24	Accurate below 11 mm.
	B (acid and alkali extd.)	3	do.	11	84	24	Accurate below 10 mm.
	M2	2	do.	14	131	43	A very good experiment.
	M3	2	do.	14	154	40	Exceptionally accurate below 13 mm.
	M4	2	do.	12	156	40	Good experiment, but points insufficient to define isothermal above 18 mm.
	G	2	do.	16	188	48	The best and the most accurate experiment. The two series gave identical linear extrapolations, with which two single-column experiments were also in agreement.
	do.	3	do.	16			
Carbon tetrachloride vapour 25°C.	B	4	33.0	37	237	41	All good experiments, the most accurate probably being that with Charcoal G.
	M3	3	do.	16	138	37	
	G	3	do.	15	140	43	

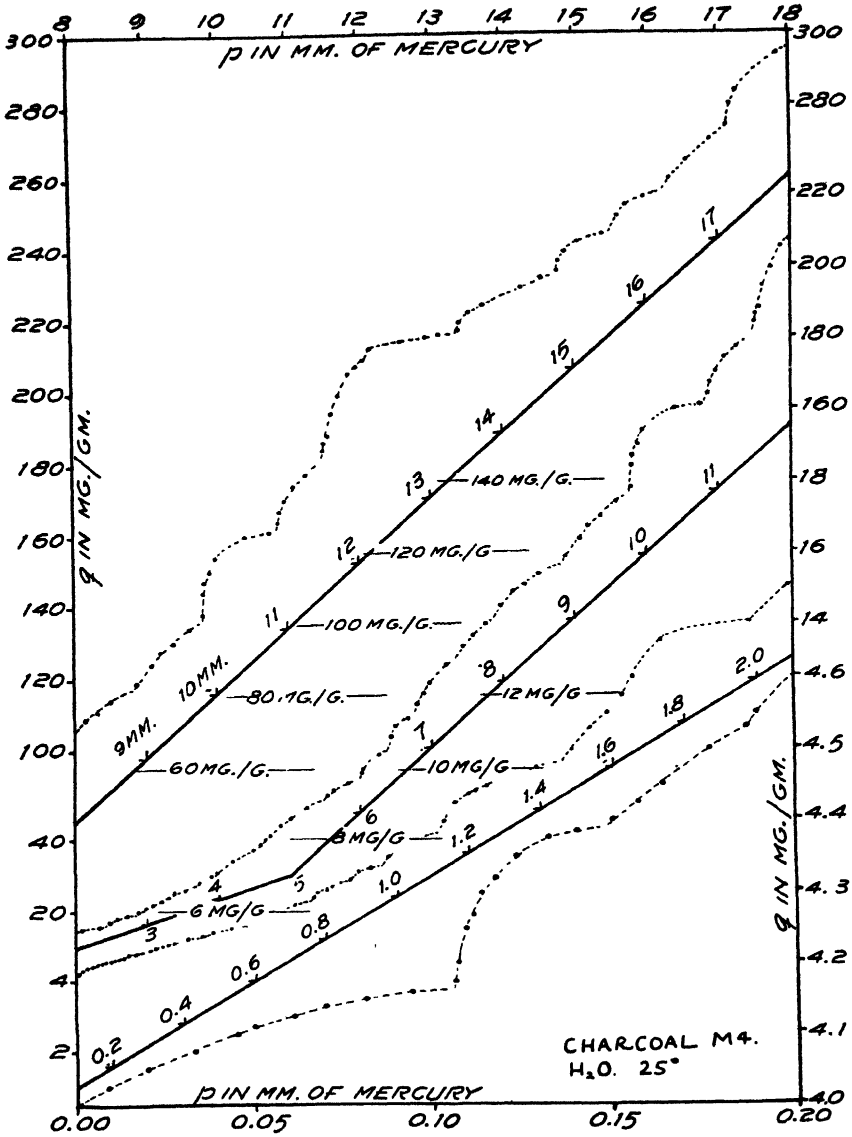

FIG. 1

than in the other cases. Several of the water isothermals showed breaks at about this pressure and some, in addition, at about 0.02 mm. We are somewhat doubtful as to their real existence.

A remarkable feature of the values of the pressures in Table II is the manner in which they appear to approximate to one or other of three fairly closely defined figures (see average values), which in turn correspond to the first three breaks. This coincidence between the pressure values is rendered still more striking by the facts (i) that the two sorbates worked with, carbon

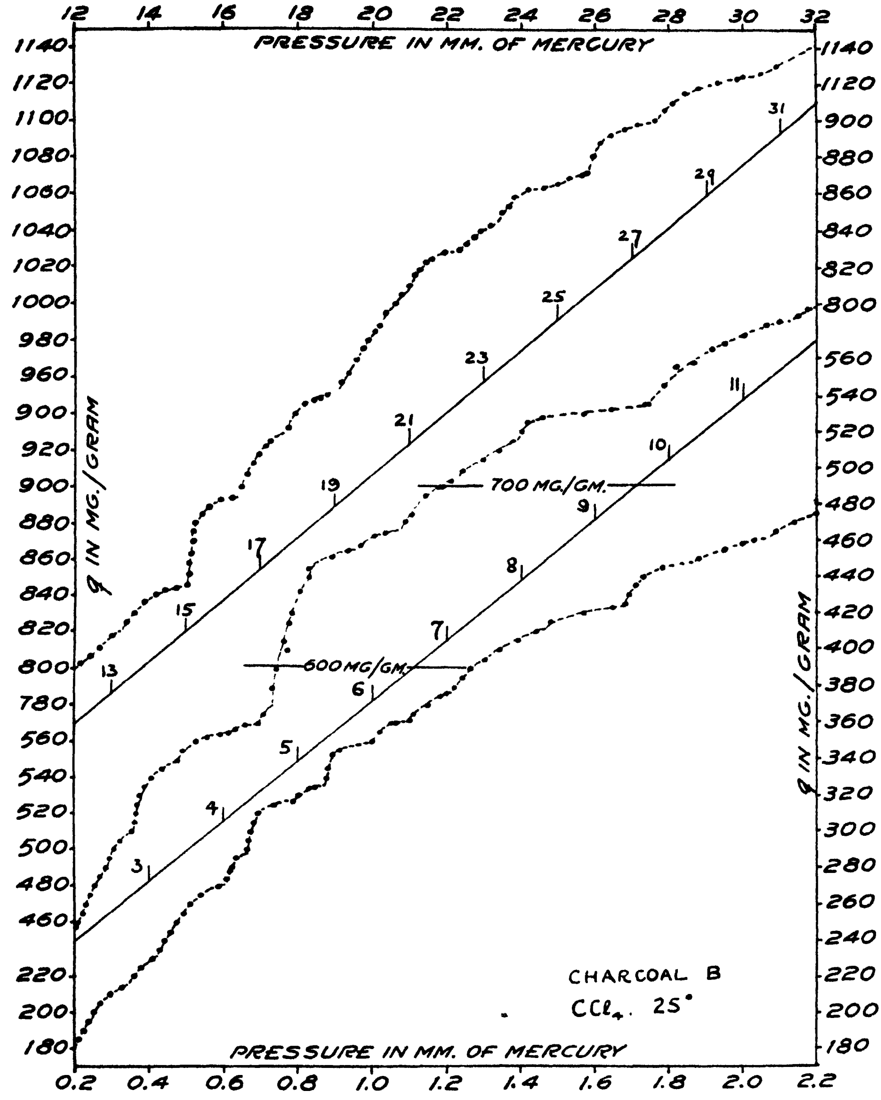

FIG. 2

tetrachloride and water, are of very different nature and furnish isothermals of quite different types and (ii) that measurements with the former substance at two different temperatures are included.

The concordance between the different pressure values very largely disappears at higher pressures. Fig. 5 contains a graphic summary of the pressures, between the limits of 5-15 mm., at which breaks have been observed during our determinations of isothermals; experiments with water vapour in which the initial charging pressure was below the latter figure are not included. The breaks are seen to vary in number from case to case, and to

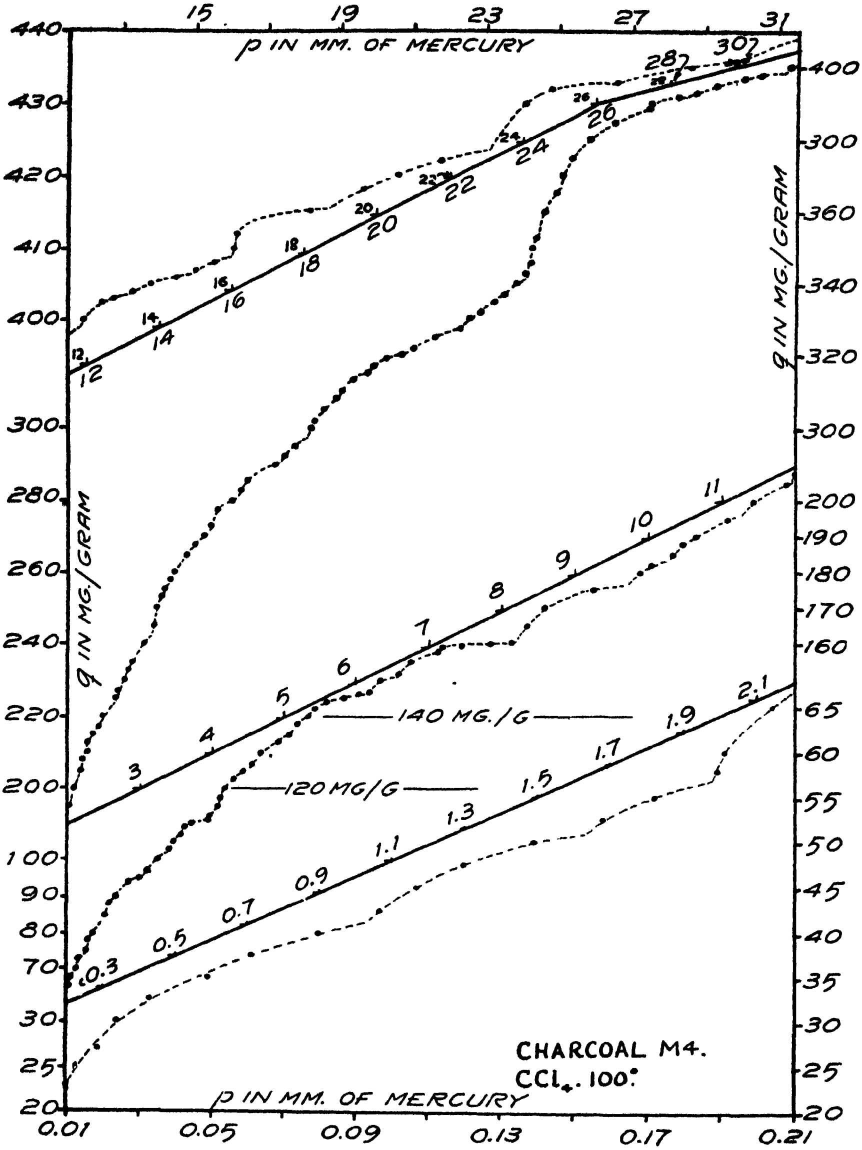

Fig. 3

be irregularly distributed. The only slight evidence of any general tendency to grouping is the fact that, above 8.9 mm., there are a number of pressure regions extending over ranges of 0.2 to 0.4 mm. within which no breaks were observed. This general lack of coincidence is emphasized by Table III (see also Fig. 4), which contains the actual data for Charcoal C over this pressure range. As far as could be judged, the experimental work appeared satisfactory in each of the three isothermal determinations concerned, and hence any

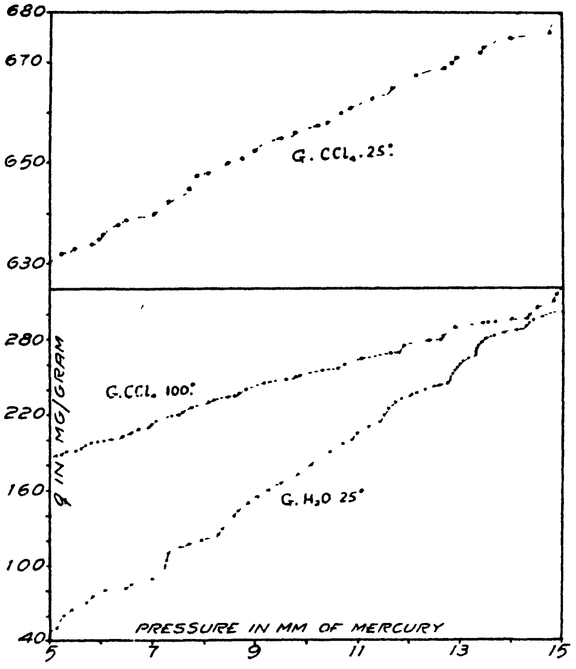

Fig. 4

Table II

	H₂O. 25°C.			CCl₄. 25°C.		
	G	(water K extd.)	M4	B	M3	G
(0.07)	0.10	0.10	0.105	0.10	0.094	0.10
	0.132	0.13	0.148	0.145	0.138	0.139
	0.175	0.18	0.187	0.192	0.190	0.17

CCl₄. 100°C.						
B	(acid B extd.)	(acid and B alkali extd.)	M2	M3	M4	G
0.11	0.10	0.095	0.11	0.11	0.095	0.11
0.156	0.154	0.15	0.15	0.144	0.150	0.138
0.185	0.174	0.18	0.183	0.180	0.188	0.187

Average figure and average deviation from mean	
0.102	(0.005)
0.144	(0.007)
0.182	(0.005)

TABLE III

Charcoal G. Pressures in mm.

H_2O	5·14	5·75	6·47	7·25	7·58	8·24	—	9·8
CCl_4 at 25°	5·35	5·93	—	7·0	7·7	8·22	8·9	9·75
CCl_4 at 100°	5·22	5·55	6·35	6·95	7·5	8·05	8·6	9·75
Mean value	5·24	5·74	6·41	7·07	7·59	8·17	8·75	9·77

H_2O at 25°	10·8	11·4	12·78	13·3	14·27	15·05
CCl_4 at 25°	10·4	11·6	12·8	13·4	—	14·8
CCl_4 at 100°	10·6	11·8	12·65	—	14·33	14·84
Mean value	10·6	11·6	12·74	13·35	14·30	14·9

tendency towards coincidence between the different pressure values should here be most marked. The table is arranged on the basis of the reality of such a tendency, and it will be seen to give some support to this assumption. Although the actual pressure figures in the vertical columns for the different isothermals differ from one another by amounts exceeding the experimental error, it is noticeable that none of the values in any one vertical column overlap those in adjacent columns. If these data be taken as supporting the existence of a tendency for the pressure values to group themselves around definite figures, then the obvious conclusion is that certain breaks have been "missed" during the determination of the isothermals.

Discussion

We shall discuss our results on the two working assumptions (i) that the "breaks" have a real existence under our experimental conditions and (ii) that they tend to occur at a definite series of pressures, depending to an unknown but secondary degree on the nature of the system and on the temperature. The first assumption we regard as well founded, the second as tentative and very open to question. An attempt has been made elsewhere[1] to suggest reasons for the existence of the alleged breaks; the present discussion will be confined to the experimental data.

As will be seen from the specimen isothermals reproduced in Figs. 1-4, the breaks differ to a great extent in degree of definition. About some, there can be no question of doubt, assuming the correctness of the experimental points. In other cases, it would appear necessary to justify the drawing of the isothermal as has been done.

A further point concerns the "missing" breaks (see Table III). Of these, there appear to be a large number. Fig. 5 covers the pressure region of 5-15 mm., and our unreproduced data, both for lower pressures with water and carbon tetrachloride, and for higher pressures with carbon tetrachloride, exhibit many instances of breaks shown in certain pressure regions by certain isothermals, but not by all. The point arises as to why breaks should be "missed" in some cases, if found in others.

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[1] In a paper submitted to the Royal Society for publication.

Lastly is the question of the degree of correspondence between the pressure values in cases where there is positive evidence that such correspondence may actually occur, e.g., in Tables II and III. If there is any concordance at all between the different pressure values, it would seem likely that any theory would demand a more regular spacing of the breaks than is found to exist, and in any case would require a degree of coincidence between the pressures falling within the average experimental error. In other words, the found degree of coincidence would be expected to be better if real, the presumption being that it may not be real. This last conclusion is the one provisionally suggested in the paper just referred to.

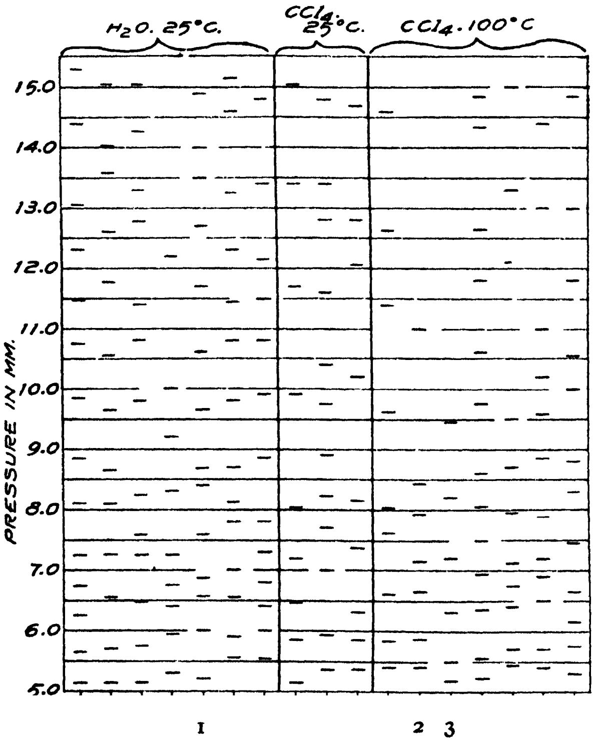

FIG. 5

(1) water extracted; (2) acid extracted; (3) acid and alkali extracted

These matters are best dealt with by a detailed analysis of the possible errors involved in our experimental method. In order to obtain the final derived isothermal, the following procedure is necessary:

(*a*) determination of the separate points in the retentivity experiment;

(*b*) their logarithmic extrapolation to figures corresponding to a column of volume 1 cc.;

(*c*) the drawing of the retentivity curve from the extrapolated data;

(*d*) the drawing and measuring of the tangents to the retentivity curve, and the construction of the derived isothermal.

These four stages will be considered in order.

(*a*) *Determination of Points in Retentivity Experiment.* The error in the weighing of the separate charcoal tubes amounted to about 0.2 mg. Expressed in mg./gram of charcoal, this is quite negligible at high *q* values, and insignificant even at quite low *q* values. The extreme limits in length of the charcoal columns were 0.5 and 12 cm. (normal figures 3-8 cm.), whilst the weight of charcoal in the separate columns normally varied between 1 and 4 grams, depending on the bulk density of the material. The times of passage of air could be determined to 0.2 second (less accurately in the earlier runs). Working at a rate of 400 cc./minute, the error for the smallest volume passed (100 cc., at the beginning of the retentivity experiment) and hence the maximum time error involved, was thus about 1.4 per cent, becoming rapidly less as the retentivity experiment proceeded. The error in the actual rate of passage of air did not exceed 2 cc./minute, or 0.5 per cent. The maximum error involved in a retentivity curve therefore amounted to about 2 per cent of the volume passed when this was small (0.1 litre), dropping to 0.5 per cent as the length of the experiment increased.

(*b*) *Extrapolation of the Experimental Points.* Each point on the final retentivity curve involves the separate weighing of the different containers which make up the composite charcoal column, and it is the results of these weighings which are extrapolated in the manner previously described. The greater that number of the charcoal containers making up the composite column, the more reliable should be the extrapolation. As will be seen from Table I, this number varied from two to six in different cases. It has been found in practice that, when once the technique of carrying out the experiments has been mastered, two columns are sufficient for a satisfactory extrapolation, the essential criterion of which is the possibility of drawing a single continuous curve through all the final points (see below).

(*c*) *The Drawing of the Retentivity Curve.* The accuracy with which this can be done depends on the number of extrapolated points obtained under (*b*), which, in its turn, depends on the number of times the retentivity experiment was interrupted for the weighing of the charcoal tubes. As will be seen from Table I, this number varied in practice between eight and thirty in the water vapour experiments, and between seven and thirty-seven in those with carbon tetrachloride. The number required to obtain a satisfactory result will of course depend on the pressure range to be covered. In the latter case, where this extended from 33 down to about 0.01 mm., we find that 16-20 points, if accurately determined, suffice for drawing a satisfactory retentivity curve, and that increasing this number makes no perceptible improvement. They must of course be suitably spaced. The fact that, in Table I, certain experiments are noted as being accurate only over certain pressure ranges, is due to faulty spacing and local inadequacy of points.

The curve itself was drawn by means of a flexible gun-metal strip, adjusted to pass through all the plotted points. If this was not possible without unnatural distortion of the strip, then an experimental error of some kind was indicated, and that portion of the curve was neglected when subsequently drawing tangents. It can not indeed be too strongly emphasized that any important error in the experimental work, leading to an uncertain extrapolation, is readily shown up when the retentivity curve is drawn.

A systematic investigation of the possible uncertainty in the final pressures (or tangent readings), due to errors in the extrapolated retentivity data of such a nature as still to permit of a continuous curve being drawn through the points, has led to the conclusion that this may conceivably amount to a *maximum* of ten per cent at low and three per cent at high, pressures. That is, a point plotted as being at 0.1 mm. may lie between 0.09-0.11 mm., and one at 30 mm. between 29-31 mm. *Neighbouring points will be subject to similar errors,* for the retentivity curve is smooth and continuous. But there is also no doubt whatever, except in the early experiments and possibly at the highest pressures, that this degree of uncertainty is usually far from being approached. On one occasion (Charcoal G; water vapour; 25 experimental points), two retentivity curves were drawn, utilising respectively the odd and even numbered extrapolated points. It was found that these curves could be superposed within experimental error. Reference may also be made to the remarks in Table I concerning the carbon tetrachloride experiments with charcoals B and G at 100.

(*d*) *The Drawing of the Tangents to the Retentivity Curve and the Construction of the Isothermal.* The actual drawing and measuring of the individual tangents involves no appreciable error if done with ordinary care. This has been amply demonstrated by constructing duplicate retentivity curves, and curves in which the extrapolated retentivity data have been plotted on more than one scale.[1] The values of the tangents to the curves at definite values of q gave pressures which were identical, or showed quite negligible differences.

It is important for absolute results to define with accuracy the initial slope of the retentivity curve, as this is a measure of the initial equilibrium pressure over the charcoal column, and subsequent pressures are calculated on the assumption of proportionality between pressure and slope. We think that our results show that errors in this initial reading are small. In any case, affecting, as they do, the pressure scale of the isothermal uniformly over its whole range, they can not account for irregular differences between the various isothermals.

One very important point however is the actual number of tangents drawn and measured. If these are not sufficiently closely spaced, as was the case in the early stages of this work, much detail in the structure of the isothermals can be missed or incorrectly plotted. In order to define the "breaks" on that part of the isothermal at intermediate pressures where its general slope is rapidly changing, some three or four points between each abrupt pressure change are necessary, and an increase beyond this number does not reveal anything fresh in the detailed isothermal structure.

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[1] Burrage: J. Phys. Chem., **34**, 2214 (1930).

If this were sufficient over the whole pressure range, then 150 tangents or thereabouts would be adequate for a carbon tetrachloride isothermal between the limits of 33 and 0.1 mm. But at lower pressures, where the general slope of the isothermal (in respect of the q axis) is small, and where the breaks, on the pressure scale, are very near one another, relatively more points are necessary for exact definition, up to as many as 10-12 on each loop of the isothermal. The same is true, to a lesser extent, of breaks which occur at high pressures, where the general slope of the isothermal is steep. In this case, the pressure range covered is so considerable that three points may be insufficient to define the path of a single isothermal loop.

The numbers of tangents actually drawn per retentivity curve are shown in Table I. There is little doubt that, although in a few cases the number was excessive, in the sense that no better definition of the isothermal was achieved than would have resulted from a smaller number, in other cases it was inadequate, over at all events a portion of the pressure range.

Conclusions

The above discussion has shown that there are four factors which may have affected the form of our final isothermals to a greater or lesser degree, *viz.*

(i) errors in the measurement of the rate of passage of air during the retentivity determinations, particularly in the earlier experiments with water vapour.

(ii) errors in the extrapolation of the retentivity points.

(iii) local insufficiency of experimental points in the retentivity experiments.

(iv) local insufficiency of tangents to the extrapolated retentivity curves.

Of these factors, we think (i) to have been of significance only in the experiments stated and (ii) seldom to have been of importance. On the other hand, it is certain that (iii) and (iv) have, in certain instances, led both to breaks remaining unnoticed, and also to the pressures of detected breaks being inexactly defined.

With regard to the question of whether or not we are justified in assuming breaks to be present in certain cases where the evidence afforded for them by the position of the points on the isothermal is obviously slender, we can only say that we have been influenced by the general nature of the particular experiments and of the subsequent extrapolation which led to the final retentivity curve. In cases where these experiments and extrapolation apparently went smoothly, as judged by the absence of any obvious hitch during their course and by the well defined nature of other parts of the isothermal, we have not hesitated to assume slight breaks on the evidence afforded by the trend of three or four adjacent points on the curve. When this was not the case, we have drawn a single loop of curve through all the points concerned.

This procedure is clearly, to a certain extent, arbitrary, but, we think, justifiable. We should indeed be prepared to find that more exact experimental methods would show a number of our supposed breaks to be non-existent. But we are inclined to think that the general result of adopting such a more refined technique would be the reverse, *viz.*, the discovery that the structure of the isothermals of vapours on charcoal is even more detailed and complex than our present work suggests it to be.

The experimental work described in this paper was carried out during the two sessions 1927-1928.

University of London,
King's College,
January 13, 1931.

THE ELECTRIC MOMENTS OF THE FIXED VEGETABLE OILS*

BY W. N. STOOPS

Introduction

Practically all the studies of dielectric polarization and electric moment of organic molecules have been carried out on pure compounds. There are, however, a large number of naturally occurring oils and resins whose chemical structure is sufficiently well established that they may be of use in furthering our knowledge of the somewhat complex relationships between molecular constitution and such properties as electric moment and dielectric constant. In addition these materials are used in the preparation of electrical insulation and hence have a practical importance.

The electric moments of these compounds were obtained from measurements of the dielectric constants and densities of dilute solutions of the oils in benzene, a non-polar solvent, the polarization at infinite dilution being calculated from them. The Debye equation may be written

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = P_E + P_A + P_O$$

where P is total polarization, ϵ the dielectric constant, M the molecular weight, d the density, P_E the electronic contribution to the polarization, P_A the atomic and P_O the contribution due to the orientation of polar molecules in the applied field. P_E is the molecular refraction preferably extrapolated to that for light of infinite wave length. P_A is usually quite small[1] in comparison with P_E and is generally neglected. P_O may be obtained as the difference between P and P_E. The electric moment of the molecule is easily obtained from P_O when the other polarization values are known, since $P_O = 4\pi N\mu^2/9kT$ where N is the Avogadro number, 6.06×10^{23}; k the gas constant per molecule, 1.372×10^{-16} ergs/degree; T the absolute temperature and μ the electric moment. The applicability of the Debye equation to dilute solutions has been amply demonstrated by Smyth[2] and Williams.[3]

Experimental

The dielectric constants were measured by means of a capacity bridge. The resistance arms were non-inductively wound and carefully adjusted to the same resistance, 1049.7 ohms. The capacity arms were General Radio variable air condensers, one their precision type 222 and the other a similarly constructed condenser without the vernier adjustment. Two General Radio variable resistances used to compensate for absorption of energy by the dielectric whose capacity was being measured were connected in series with the condensers. Each unit was individually shielded in accordance with the principles laid down by Campbell[1] and developed by the Bell Telephone Laboratories.[2]

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*Sci. Paper No. 487.

[1] C. P. Smyth: J. Am. Chem. Soc., **51**, 2051 (1929).

[2] Smyth, Morgan and Boyce: J. Am. Chem. Soc., **50**, 1536 (1928).

[3] J. W. Williams: Physik. Z., **29**, 174 (1928).

The oscillator, built on a slightly modified Hartley circuit, was mounted in a shielded box. It was calibrated at 300,000, 600,000 and 1,000,000 cycles by means of a wave meter and the frequency checked from time to time. The detector was mounted in a separate shielded box and consisted of a crystal detector and a high sensitivity galvanometer. It was similar to the one described by Smyth, Morgan and Boyce.

The measuring condenser or cell for the measurement of dielectric constants of liquids consisted of three concentric brass cylinders, heavily gold plated and separated by small mica tabs. The condenser was mounted in a glass tube with a separate platinum wire for each cylinder coming out through capillary tubing. Three combinations giving three different capacities were possible, the only restriction being that the outer cylinder was always kept grounded to serve as a shield. This cell was calibrated with carefully purified benzene, using the value of 2.273 at 25°C for the dielectric constant[3] of benzene. The densities were measured with a pycnometer somewhat similar to that used by Isnardi.[4]

A large Dewar tube filled with toluene served as a constant temperature bath. The low temperatures were obtained by the use of liquid air[5] and those above room temperature by means of a small heating coil. The temperature of the bath was held constant to ±.05°C for ten minutes for the dielectric constant measurements and fifteen to twenty minutes for the density determinations. The probable error in the densities measured at low temperatures was 0.07% and in those above 0° not more than 0.03%. The dielectric constants were measured by direct substitution of the gold plated cell on the precision condenser. The probable error was 0.2% although the error within a given series of measurements was less. When several ohms resistance was necessary in the balancing arm to compensate for conductance or absorption in the cell the dielectric constants are probably not accurate to more than 1%. These resistances were necessary only for the pure oils at low temperatures, the dilute solutions of the oils in benzene showing no absorption. The effect of the resistance was to cause the apparent values of the dielectric constants to be too large.

Materials

Castor Oil. Baker's best grade of cold pressed castor oil was used without purification.

$d_{4^\circ}^{20^\circ} = .9613 \quad n^{27.5^\circ} = 1.4770$; (where n = refractive index)

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[1] G. A. Campbell: Elec. World, **1904**, 647.

[2] W. J. Shackelton: Bell Sys. Tech. J., **6**, 142 (1927).

[3] Hartshorn and Oliver: Proc. Roy. Soc., **123**, 664 (1929).

[4] Isnardi: Z. Physik, **9**, 153 (1922).

[5] See Walters and Loomis: J. Am. Chem. Soc., **47**, 2302 (1925).

Linseed Oil. Commercial raw oil was used which had been heated for an hour at 150°C. The heating precipitates a certain amount of impurities in the oil but does not appreciably polymerize it. $d^{20°}_{4°} = .9366$; $n^{15.0°} = 1.4860$.

Tung Oil. The tung oil was the commercial product of the quality used in the electrical industry.

$$d^{20°}_{4°} = .9394;\ n^{23.0°} = 1.519$$

Tristearin. Eastman's C. P. tristearin was used without further purification.

Benzene. Fisher Scientific Company C. P. benzene was washed three times with sulfuric acid, then with dilute sodium carbonate solution and with water, dried over calcium chloride and fractionally crystallized. It was then dried over sodium and fractionally distilled.

Experimental Results

The densities, which showed only slight departure from a linear variation with temperature, were measured at 20° intervals and the dielectric constants at about 10° intervals. The densities d and dielectric constants ε in Table I

TABLE I

Interpolated values of dielectric constants and densities and the polarizations calculated from them

	Tung Oil			Linseed Oil			Castor Oil		
t°c	d	ε	P	d	ε	P	d	ε	P
−70				1.00	2.48	281	1.0242	2.55	310
−60				1.00	2.55	290	1.0172	2.65	326
−50		2.51		.9955	2.80	320	1.0102	2.79	345
−40	.9821	2.54	304	.9863	3.32	376	1.0033	3.00	372
−30	.9750	3.19	381	.9771	3.46	392	.9964	3.52	428
−20	.9680	3.33	398	.9679	3.50	399	.9893	4.12	480
−10	.9609	3.42	409	.9590	3.50	403	.9823	4.58	517
0	.9537	3.43	413	.9512	3.49	406	.9753	4.71	529
+10	.9466	3.41	414	.9436	3.45	405	.9683	4.71	533
20	.9394	3.37	413	.9366	3.40	403	.9613	4.66	533
30	.9323	3.33	412	.9298	3.35	402	.9543	4.54	530
40	.9253	3.29	411	.9229	3.31	400	.9472	4.44	526
50	.9185	3.26	409	.9159	3.26	398	.9402	4.33	522
60	.9116	3.19	407	.9090	3.22	397	.9332	4.23	519
70	.9048	3.14	405	.9021	3.17	396	.9262	4.13	515
80	.8978	3.10	403	.8952	3.13	395	.9191	4.03	511
90	.8908	3.06	402	.8883	3.08	393	.9119	3.94	507
100	.8838	3.02	400	.8814	3.04	390	.9046	3.84	502

were obtained at 10° intervals by graphical interpolation, and the polarizations P were calculated from them by means of the Debye equation given above. In Table II are given the mole fractions, C_2, of the polar constituents, the densities and dielectric constants of the solutions and the polarizations P_{12} and P_2 calculated from them by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{C_1M_1 + C_2M_2}{d} \text{ and } P_2 = \frac{P_{12} - P_1}{C_2} + P_1$$

Here P_{12} is the polarization of the mixture, and C_1 and C_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the two components.

TABLE II

C_2	d	ϵ	P_{12}	P_2
		Tung Oil. 25° C. $P_1 = 26.57$		
.003088	.8754	2.306	27.90	457
.004583	.8762	2.323	28.53	454
.006370	.8773	2.341	29.28	452
.009460	.8790	2.368	30.49	441
.012386	.8805	2.396	31.73	443
.024186	.8859	2.437	35.62	401
		Linseed Oil 27°C. $P_1 = 26.59$		
.004872	.8721	2.319	28.65	450
.007782	.8756	2.351	29.81	441
.009824	.8767	2.367	30.58	432
.012442	.8778	2.391	31.69	437
.016000	.8795	2.420	33.02	429
		Castor Oil 30°C. $P_1 = 26.68$		
.002695	.8702	2.312	28.09	551
.004168	.8713	2.340	28.92	564
.005760	.8733	2.366	29.75	560
.008250	.8749	2.410	31.10	563
.010293	.8764	2.442	32.17	560
		Tristearin 35°C. $P_1 = 26.70$		
.003803	.8634	2.281	28.12	416.1
.004160	.8632	2.287	28.32	416.1
.004410	.8636	2.291	28.44	421.3
.004595	.8634	2.292	28.51	420.6

Discussion

The density varies practically linearly with temperature, and this same variation is assumed to hold at temperatures below the melting point, they having been obtained by extrapolation. The oils showed a marked tendency to super-cool, but had usually completely solidified at −40° or above. In Fig. 1 the dielectric constants of the three oils are plotted against temperature. The pronounced falling off in dielectric constant at low temperatures is due to the fact that the polar molecules are no longer able to orient in the field, and hence the dipole contribution to the dielectric constant disappears. For linseed oil and tung oil solidification occurs at about −25° and −10° respectively, but the freezing point is not sharp and hence the dielectric constant drops gradually from the value for the liquid to that for the solid. The points on the steepest part of the curves depend on whether they are measured on oil that is freezing or melting, indicating that the ten to fifteen minutes at constant temperature before each reading is not long enough for attaining a true equilibrium. The castor oil supercooled, and did not solidify even at the lowest temperature with the result that all parts of the curve were reproducible. Although the oil did not solidify, the increase in viscosity is sufficient to interfere with and finally to practically prevent the orientation of the dipoles. The gradual decrease in freedom of orientation of the dipoles caused by the increase of viscosity results in a smoother and less abrupt falling off in the dielectric constant than in the other two oils where solidification occurs. The polarizations of the oils exhibit almost the same variation with temperature as the dielectric constants, going through a maximum at about 10°C, then decreasing slowly at higher temperatures and rapidly at lower ones.

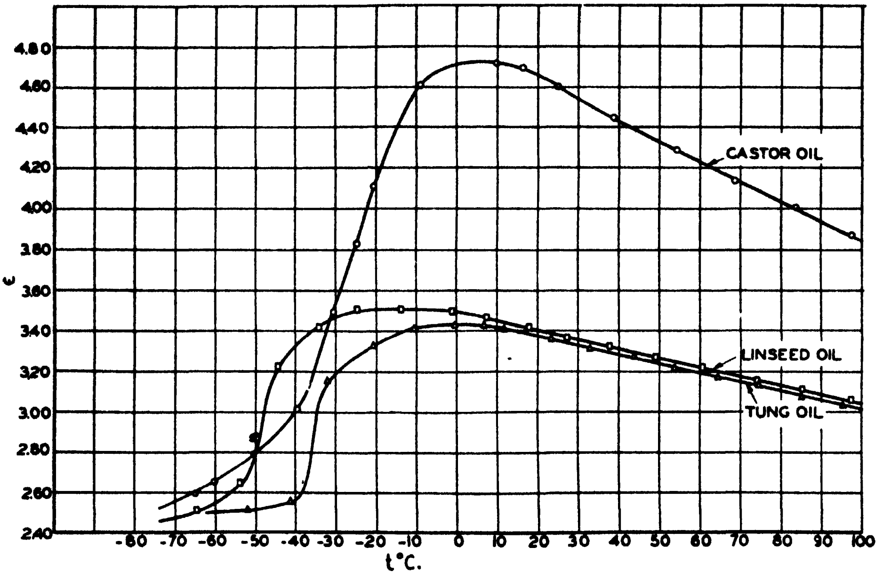

Fig. 1

TABLE III

Values of Polarization Terms

Substance	Temp.	P_∞	P_2	P_E	P_S	P_O	$\mu \times 10^{18}$
Tung Oil	25°	461	413	286	306	165	2.8
Linseed Oil	27°	457	402	260	280	187	3.0
Castor Oil	30°	564	530	276	300	276	3.7
Tristearin	35°	419		272		147	2.7

The polarization values and electric moments for the three oils and for tristearin are given in Table III. The polarization at infinite dilution, P_∞, was obtained by plotting P_2 against the concentration C_2 and extrapolating to zero concentration. The temperature given applies only to P_∞ and P_2, the polarization of the pure oils, the other terms being independent of temperature. The polarization of the solid, P_S, was calculated from the dielectric constant obtained by freezing the liquid in the cell, and from the density got by extrapolating from the liquid to the solid state, assuming the same variation with temperature. The contraction on solidification probably prevents the oil from entirely filling the space between the cylinders in the measuring condenser, and causes the measured dielectric constant to be too low. Nevertheless, it may be noted that the P_S values are all about twenty units higher than the corresponding molecular refractions, an increase which is about what we would expect for the atomic refraction P_A.[1] The molecular refractions P_E, were determined from refractive index data obtained from the literature for tristearin, and by a Pulfrich refractometer for the oils. The orientation polarization, P_O, was taken as the difference between P_∞ and the average of P_E and P_S, except in the case of tristearin for which P_S was not measured.

The magnitude of all these quantities depends of course upon the molecular weight of the material. Tristearin is a pure compound and has a definite molecular weight, but the oils are mixtures and an approximate value must be assigned. The composition of tung oil is fairly well known,[2] it being about 80-85% trielaeosterine of molecular weight 878.9 and 15-20% triolein of molecular weight 885.1. The value of 880 was used for the molecular weight of tung oil in these calculations, and cannot be much in error. The molecular weight of the linseed oil used was taken as 850. A theoretical figure assuming it to be entirely triglyceride of its various acid constituents would be 875-885, but it contains some mono- and diglycerides. An analysis of linseed oil by Eibner and Schmidinger[3] shows it to consist of triglycerides of linolic acid, 60%, linolenic 23%, saturated acids 8%, and oleic acid 5%. Linolenic acid differs from linolic (whose triglyceride is shown in Fig. 2) in that it contains three double bonds in each carbon chain instead of two. Experimentally determined molecular weights vary from 750 to 850 for raw oil. The oil used had been heated slightly (an hour at 150°-200° to remove a precipitate which forms in the early stages of heating) but not sufficiently to appreciably polymerize it. Castor oil is about 80% triglyceride or ricinoleic acid[4] with small proportions of the triglycerides of similar acids. The molecular weight was taken as 933, that of the principal constituent of the oil.

A fairly long chain acetate molecule, such as amyl, has a moment of 1.9.[5] A glyceride may be considered as three such acetate molecules connected at one end, although of course not all to the same carbon atom. If the three

[1] C. P. Smyth: J. Am. Chem. Soc., 51, 2051 (1929).

[2] Wissensch. Veröffent. dem Siemens-Konzern. Vol. IV, Pt. 2 p. 284 (1925).

[3] Eibner and Schmidinger: Chem. Umschau, 30, 293 (1923).

[4] Eibner and Munzing: Chem. Umschau, 32, 153 (1925).

[5] Müller and Sack: Physik. Z., 31, 815 (1930).

groups in the glyceride molecule lie parallel and exert no influence the one on the other a molecule such as tristearin should have a moment of 3 times 1.9 or 5.7. The moment found, 2.7, shows that the interaction of the dipoles is quite strong. Adam[1] has shown that the area per chain of tristearin as a close-packed film is the same as the area of the stearic acid molecule, indicating that the chains are parallel to each other. However in dilute solution where the molecules are comparatively far apart the repulsive forces between the dipoles must separate the chains and produce the smaller moment for the molecule as a whole.

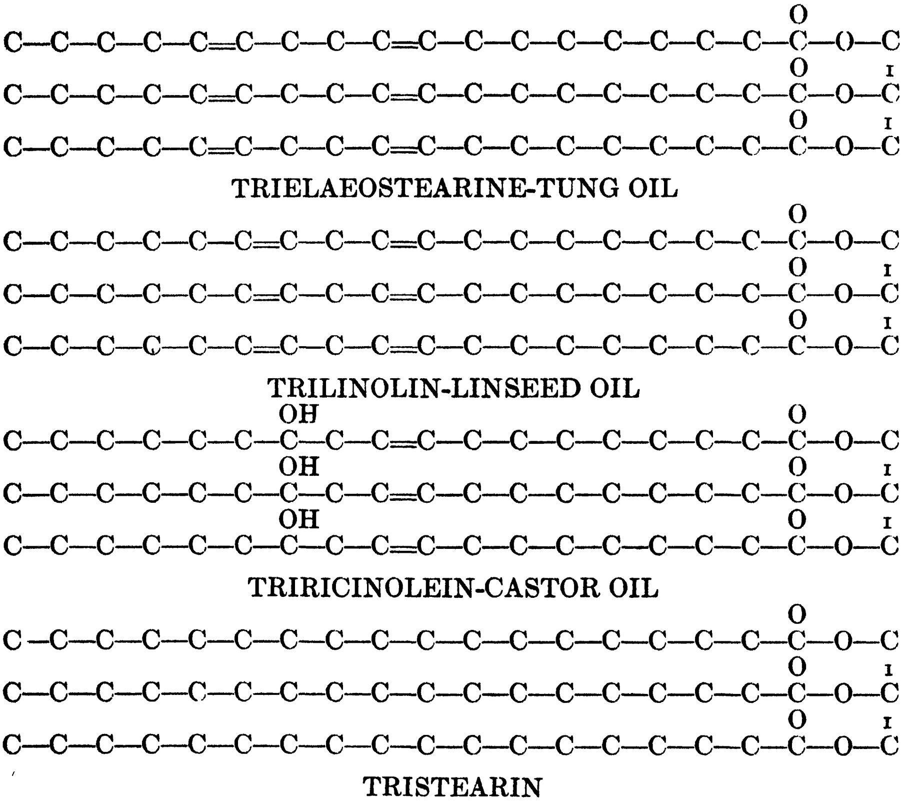

FIG. 2
Formulae of tristearin and of the principal constituents of the oils.

The structural formulae of tristearin and of the chief constituent of each of the oils are given in Fig. 2, the hydrogen atoms being omitted. The oils may evidently be considered as derivatives of tristearin, tung and linseed oils differing only by the presence of six double bonds in the carbon chains, and castor oil by three double bonds and three hydroxyl groups. A small but definite polarity is known to be associated with the double bond[2] when it is unsymmetrically located in the molecule. Hence it is not surprising that tung and linseed oils have slightly larger moments than tristearin. The slight difference in the location of the double bonds in the two oils can scarcely account for their differences in moment. Linseed oil contains several other constituents in small proportion in addition to that whose structure is given in Fig. 2 and some of them may be of a more highly polar nature. Furthermore, the molecular weight assigned to the oil may be sufficiently in error to account for the difference in moment.

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[1] Adam: "The Physics and Chemistry of Surfaces," 50 (1930).

[2] Smyth and Zahn: J. Am. Chem. Soc., 47, 2501 (1925).

Bless[1] has obtained a value of 2.19_5 for the moment of tung oil. There is not sufficient information in the abstract to determine whether the difference between this value and the one given above is due to a smaller molecular weight for tung oil or to some other cause. That tung oil should have a moment less than 2.7, that of tristearin, seems very unlikely on consideration of the close structural resemblance of their molecules.

Castor oil contains in addition to the double bond an hydroxyl group attached to each of the long carbon chains. The hydroxyl group has a moment of 1.7 and should increase the polarity of the triglyceride molecule, and the value of 3.7 is no larger than would be expected.

The so called "fixed" vegetable and animal oils and fats consist chiefly of triglycerides.[2] The most common acids from which the glycerides are formed are stearic, oleic, palmitic, linolic, and hydroxy acids.' The substances studied here cover the range fairly thoroughly, castor oil containing the hydroxy and dihydroxy esters, linseed oil and tung oil the unsaturated ones and tristearic the completely saturated ester. Therefore it seems reasonably certain the moments of the other animal and vegetable oils and fats of this class will have moments in the same range, from 2.7 to 3.7, depending on the constitution of the acids of which they are composed.

Summary

The dielectric constants and densities of three vegetable oils, namely tung oil, linseed oil and castor oil, have been measured over a wide temperature range and their polarization calculated.

The electric moments of these oils and of tristearin were obtained by means of measurements on their dilute solutions in benzene and are 2.7, 2.8, 3.0 and 3.7×10^{-18} e.s.u. for tristearin, tung oil, linseed oil and castor oil respectively. The values are discussed from the standpoint of the molecular structure of the compounds.

These oils are typical of the group of fixed oils and fats of the triglyceride structure and they may all be expected to have electric moments varying from 2.7 to 3.7.

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[1] Bless: Phys. Rev., **35**, 1442 (1930).

[2] See, for instance, Thorpe: "Dictionary of Applied Chemistry," **4**, 645.

SURFACE TENSION OF SATURATED VAPORS AND THE EQUATION OF EÖTVÖS

BY J. L. SHERESHEFSKY

In discussing phenomena of solid-liquid or liquid-liquid surfaces it is usually emphasized that the properties under consideration belong to neither of the phases making up the interface, but to the interface proper. Thus it is made clear that the tension in a benzene-water interface is characteristic, neither of the benzene, nor of the water, but of the new phase of the interface which is made up of the latter two. But there is generally a lack of definiteness when dealing with liquid surfaces in contact with their own vapors. The properties of such surfaces are usually ascribed to the liquids concerned, without giving due consideration to the effect that the respective vapor phases undoubtedly have on these properties.

Van der Waals was the first to point out that the surface represents a third phase whose properties differ from those of the liquid or vapor. There is thus a complete parallelism between liquid-liquid and liquid-vapor interfaces. The surface tension, say, of benzene is therefore understood to refer neither to the liquid benzene, nor to the benzene vapor, but to the benzene (liquid)-benzene (vapor) interface, and is also conceived as the resultant of two effects produced by the surfaces presented by the liquid and the vapor.

The Surface Tension of Saturated Vapors

The tension in a liquid-liquid interface as determined by the method of capillary rise is given by the expression

$$\sigma = \tfrac{1}{2} r\, h\, g\, (\rho_1 - \rho_2) \qquad (1)$$

where h is the height of rise, r the radius of the capillary, and ρ_1 and ρ_2 the densities of the immiscible liquids in equilibrium with each other. This expression also holds for the interface between a liquid and its vapor, ρ_1 and ρ_2 being the respective densities.

It is therefore evident that the tension of a surface formed by the contact of two fluid phases, whether they be two immiscible liquids, or a liquid and its vapor, is given by the difference of two terms, and thus is analogous to Antonoff's[1] rule, which states that the interfacial tension between two liquids is equal to the difference of the surface tensions of the liquids in equilibrium with each other. Thus, if σ is the relative, or interfacial tension, σ_1 the surface tension of liquid (1) in equilibrium with the vapor of liquid (2), and σ_2 is the surface tension of liquid (2) in equilibrium with the vapor of (1), Antonoff's rule may be expressed by the equation

$$\sigma = \sigma_1 - \sigma_2 \qquad (2)$$

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[1] Phil. Mag., (6) **36**, 377 (1918).

Applying this rule to an interface between a liquid and its vapor σ represents the relative surface tension, σ_1 the tension of the liquid surface proper, that is, of a hypothetical liquid surface whose vapor was momentarily removed or frozen, and σ_2 is the tension of the surface presented by the vapor. From this follows by analogy that

$$\sigma_1 = \tfrac{1}{2}\,\mathrm{rhg}\rho_1 \qquad (3)$$

and

$$\sigma_2 = \tfrac{1}{2}\,\mathrm{rhg}\rho_2 \qquad (4)$$

A more rigorous derivation of these equations may be obtained from considerations of equation (1) as applied to liquid surfaces in contact with vapors. At temperatures far removed from the critical the vapor density term, ρ_2, is usually omitted, since it is negligible with respect to the density of the liquid. As a result equation (1) becomes only approximate and assumes the more simplified form of

$$\sigma = \tfrac{1}{2}\,\mathrm{rhg}\rho_1 \qquad (5)$$

This expression increases in accuracy at lower temperatures, and becomes exact as the vapor pressure of the liquid approaches zero. At this state of the liquid the relative surface tension, σ, becomes equal to the absolute tension, σ_1, of the liquid surface proper. Since this state also corresponds to the hypothetical liquid surface postulated above equation (5) becomes identical with equation (3), which defines the absolute surface tension of a liquid.

The surface tension of a vapor as defined in equation (4) may now be obtained by combining equation (3) with the expression for the relative surface tension of a liquid as given by equation (1), and with equation (2) expressing Antonoff's rule.

Entirely different consideration led N. Barbulescu[1] to the same conclusions.

The Surface Tension of Saturated Vapors and Temperature

To relate the surface tension of saturated vapors to temperature the following two equations are utilized.

$$\sigma = \mathrm{K_1T_cV^{-\frac{2}{3}}}\,(1 - \mathrm{T/T_c})^{1.2} \qquad (6)$$

and

$$\rho_1 - \rho_2 = \mathrm{K_2}\rho_c\,(1 - \mathrm{T/T_c})^{0.3} \qquad (7)$$

Equation (6) was deduced by van der Waals from his theory of corresponding states, and later modified by S. Sugden.[2] Equation (7) was suggested by D. H. Goldhammer[3] and corrected by S. Sugden[4]. Here $\mathrm{T_c}$ and ρ_c are the critical temperature and critical density respectively, V the molar volume of the liquid, and K_1 and K_2 constants which are approximately universal for all non-polar liquids.

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[1] Physik. Z., **31**, 48 (1930).

[2] J. Chem. Soc., **125**, 32 (1924).

[3] Z. physik. Chem., **71**, 577 (1910).

[4] J. Chem. Soc., **130 II**, 1780 (1927).

Combining these with equations (1) and (4), we obtain the expression

$$\sigma_2 = \frac{\Delta T_c}{\rho_c^{1/3} M^{2/3}} (1 - T/T_c)^{0.9} \rho_2 \tag{8}$$

which relates the surface tension of saturated vapors to the density of the vapor, its critical constants and temperature. The constant Δ equals K_1/K_2 and is nearly the same for all non-associated substances, M is the molecular weight, and the other terms have the designated significance.

To test the validity of this equation the surface tension of the saturated vapors of six liquids at various temperatures were calculated and compared with observed values. The agreement as shown in Tables I to VI inclusive is very good up to the critical temperature for all substances except carbon

TABLE I

Surface Tension of Saturated Vapors

Benzene

$\Delta = 1.39$ Mol. Wt. = 78.05; $T_c = 561.5$ $\rho_c = .3045$

I t°C	II $1 - T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	VI Percent Deviation
90	.353	.0036	.0904	.0935	3.43
120	.302	.0076	.1640	.1640	0.00
150	.247	.0144	.262	.260	0.76
180	.193	.0249	.357	.360	0.84
210	.140	.0421	.453	.456	0.66
240	.086	.0715	.483	.498	3.11
280	.016	.2209	.344	.340	1.16

TABLE II

Surface Tension of Saturated Vapors

Chlorobenzene

$\Delta = 1.39$ Mol. Wt. = 112.5; $T_c = 632.2$ $\rho_c = .3654$

I t°C	II $1 - T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	VI Percent Deviation
150	.332	.0054	.105	.1057	0.67
180	.283	.0102	.172	.173	0.58
210	.236	.0180	.253	.258	1.98
240	.188	.0301	.348	.353	1.44
270	.141	.0494	.433	.446	3.00
300	.093	.0778	.490	.485	1.02
320	.062	.1075	.456	.465	1.98
333	.042	.1360	.450	.415	7.78

Table III

Surface Tension of Saturated Vapors

Ethyl Ether

$\Delta = 1.39$ Mol. Wt. $= 74.1$; $T_c = 466.8$ $\rho_c = 0.2625$

I t°C	II $1-T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	VI Percent Deviation
20	.373	.00187	.0447	.0442	1.12
50	.308	.00508	.1037	.1013	2.32
80	.245	.01155	.1880	.1875	0.27
110	.179	.02349	.2880	.2870	0.35
140	.114	.04448	.3610	.3610	0.00
170	.049	.08731	.3280	.331	0.91
185	.017	.1320	.1960	.194	1.02

Table IV

Surface Tension of Saturated Vapors

Carbon Tetrachloride

$\Delta = 1.39$ Mol. Wt. $= 153.84$; $T_c = 556.2$ $\rho_c = 0.5576$

I t°C	II $1-T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	VI Percent Deviation
90	.3475	.0079	.1010	.0995	1.49
120	.293	.0163	.1770	.1765	0.28
150	.239	.0302	.2683	.2720	1.38
180	.185	.0525	.3730	.3780	1.34
210	.132	.0879	.4660	.465	0.22
240	.077	.1464	.4300	.477	10.95
270	.0225	.2710	.222	.298	34.20

Table V

Surface Tension of Saturated Vapors

Methyl Formate

$\Delta = 1.31$ Mol. Wt. $= 60.04$; $T_c = 487$ $\rho_c = 0.3489$

I t°C	II $1-T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	IV Percent Deviation
50	.337	.0043	.095	.0955	0.53
80	.275	.0105	.193	.1943	0.67
110	.2125	.0216	.316	.317	0.28
140	.152	.0412	.438	.447	2.06
170	.090	.0763	.497	.516	3.83
200	.028	.1524	.340	.361	6.18

TABLE VI

Surface Tension of Saturated Vapors

Ethyl Acetate

$\Delta = 1.43$ Mol. Wt. = 88.06; $T_c = 523.1$ $\rho_c = 0.3077$

I t°C	II $1-T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	VI Percent Deviation
90	.307	.0047	.0918	.0907	1.20
120	.248	.0103	.1645	.1643	0.12
150	.192	.0206	.260	.260	0.00
180	.134	.0388	.353	.346	2.76
210	.077	.0712	.400	.396	1.00
240	.019	.1500	.229	.237	3.49

tetrachloride. In the latter case the divergence is most probably due to the doubtful data in the neighborhood of the critical temperature. The observed values in the fourth column of each table were taken from the data of Ramsay and Shields as recalculated and corrected by S. Sugden.[1]

It is to be observed that the surface tension of saturated vapors attains a maximum value near the critical temperature, the ratio of the temperature at which the maximum occurs to the critical temperature being the same for all substances, as was shown by the author in a preceding paper.[2]

The Law of Eötvös

To express the relationship between surface tension of a liquid-vapor surface and temperature Eötvös suggested, in analogy to the gas law PV = RT, the similar equation

$$\sigma(M/\rho_1)^{2/3} = K(T_c - T) \tag{9}$$

As this equation was only exact for low temperatures and was far from reproducing the experimental results for the whole range of temperatures up to the critical, Ramsay and Shields have introduced after an extensive investigation an arbitrary constant "d", thus modifying the equation to the form

$$\sigma(M/\rho_1)^{2/3} = K(T_c - T - d) \tag{10}$$

This equation, while it has improved upon the Eötvös equation in accuracy, has lost its symmetry and is not consistent with the theory of corresponding states. It furthermore shares, with the original Eötvös equation, the fault that it takes no consideration of the density of the vapor, which has as it was shown above an important effect upon the surface tension of the interface.

A relationship which shall be consistent with the theory of corresponding states, and which shall also take account of the vapor density, may be developed on the basis of the conclusions arrived at in the preceeding section in this paper.

[1] J. Chem. Soc., **125**, 32 (1924).

[2] J. Phys. Chem., **34**, 1947 (1930).

Combining equations (1) and (4), we obtain

$$\sigma_2 = \sigma\left(\frac{\rho_2}{\rho_1 - \rho_2}\right) \tag{11}$$

which relates the relative surface tension, σ, with the surface tension of the vapor, σ_2. Substituting for the latter its equivalent in equation (8), we obtain

$$\sigma\left(\frac{M^{2/3}}{\rho_1 - \rho_2}\right) = \triangle \frac{T_c}{\rho_c^{1/3}} (1 - T/T_c)^{0.9} \tag{12}$$

which in multiplying by $(\rho_1 - \rho_2)^{1/3}$ assumes a form that is very similar to the original expression of Eötvös' Law, namely

$$\sigma\left(\frac{M}{\rho_1 - \rho_2}\right)^{2/3} = \triangle T_c\left(\frac{\rho_1 - \rho_2}{\rho_c}\right)^{1/3} (1 - T/T_c)^{0.9} \tag{13}$$

A similar relationship was suggested by N. Katayama[1] as shown by equation (14)

$$\sigma\left(\frac{M}{\rho_1 - \rho_2}\right)^{2/3} = K(T_c - T) \tag{14}$$

This equation accounts for the vapor density as well as equation (13), but is not as complete in its relationship to the theory of corresponding states, since the latter includes the critical volume as well as the critical temperature. It is also not in as good agreement with experiment, as equation (13), as is evidenced in Tables VII to XII inclusive. The values of σ calculated by

TABLE VII

The Equation of State for Liquid-Vapor Interfaces

Benzene (liquid)-Benzene (vapor)

$\triangle = 1.39$ Mol. Wt. = 78.05 $T_c = 561.5$ $\rho_c = .3045$

I t°C	II $1 - T/T_c$	III $\rho_1 - \rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
13.5	.490	.8857	29.72	29.70	
20.5	.477	.8782	28.91	28.86	
32.5	.456	.8653	27.30	27.20	
39	.445	.8581	26.36	26.40	
41.5	.439	.8553	26.08	26.00	
54.8	.417	.8400	24.28	24.38	
61	.406	.8330	23.61	23.60	
.72	.386	.8207	22.15	22.70	
90	.353	.8006	20.13	20.00	19.08
120	.302	.7616	16.42	16.52	15.67
150	.247	.7166	13.01	12.98	12.37
180	.193	.6657	9.56	9.65	9.22
210	.140	.6011	6.45	6.53	6.23
240	.086	.5137	3.47	3.60	3.47
270	.033	.3696	1.05	1.09	1.06
280	.016	.2305	0.36	0.36	0.36

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[1] Tohoku Imp. Univer. Science Reports, (1) **4**, 373 (1916).

TABLE VIII

The Equation of State for Liquid-Vapor Interfaces

Chlorobenzene (liquid)-Chlorobenzene (vapor)

$\Delta = 1.39$ Mol. Wt. = 112.5; $T_c = 632.2$ $\rho_0 = .3654$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
12	.549	1.118	34.36	34.40	
18.7	.538	1.108	33.35	33.50	
24.1	.523	1.102	32.85	32.40	
41	.503	1.083	30.78	30.85	
50	.488	1.073	29.83	29.70	
62.1	.470	1.059	28.20	28.40	
81	.440	1.039	26.10	26.25	
93	.422	1.025	24.99	24.90	
123	.373	.9910	21.63	21.53	
150	.332	.9545	18.55	18.65	17.57
180	.283	.9122	15.40	15 50	14.61
210	.236	.8622	12.16	12.38	11.71
240	.188	.8054	9.30	9.45	8.94
270	.141	.7341	6.43	6.63	6.29
300	.093	.6442	4.05	4.01	3.83
320	.062	.5628	2.39	2.43	2.32
333	.042	.4914	1.63	1.50	1.41

TABLE IX

The Equation of State for Liquid-Vapor Interfaces

Ethyl Ether (liquid)-Ethyl Ether (vapor)

$\Delta = 1.39$ Mol. Wt. = 74.1; $T_c = 466.8$ $\rho_0 = 0.2625$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
20	.373	.7109	17.01	16.80	16.12
50	.308	.6713	13.69	13.35	12.81
80	.245	.6286	10.25	10.20	9.71
110	.179	.5707	7.00	6.97	6.81
140	.114	.4936	4.00	4.01	3.97
170	.049	.3785	1.42	1.44	1.47
185	.017	.2698	0.40	0.40	0.46

TABLE X

The Equation of State for Liquid-Vapor Interfaces

Carbon Tetrachloride (liquid)-Carbon Tetrachloride (vapor)

$\Delta = 1.39$ Mol. Wt. = 153.84; $T_c = 556.2$ $\rho_c = 0.5576$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
20	.473	1.593	26.95	26.60	25.55
33	.450	1.567	25.22	25.00	
45.9	.426	1.540	23.63	23.40	
90	.3475	1.4475	18.51	18.25	17.59
120	.293	1.3740	14.95	14.90	14.35
150	.239	1.2914	11.46	11.62	11.24
180	.185	1.1945	8.50	8.60	8.27
210	.132	1.0687	5.67	5.66	5.44
240	.077	0.8980	2.64	2.92	2.86
270	.0225	0.5955	0.49	0.66	0.56

TABLE XI

The Equation of State for Liquid-Vapor Interfaces

Methyl Formate (liquid)-Methyl Formate (vapor)

$\Delta = 1.31$ Mol. Wt. = 60.04; $T_c = 487$ $\rho_c = 0.3489$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
50	.337	.9251	20.48	20.52	19.96
80	.275	.8698	15.95	16.10	15.68
110	.2125	.8048	11.77	11.80	11.55
140	.152	.7156	7.63	7.77	7.65
170	.090	.6081	3.96	4.12	4.06
200	.028	.4131	0.92	0.98	1.00

TABLE XII

The Equation of State for Liquid-Vapor Interfaces

Ethyl Acetate (liquid)-Ethyl Acetate (vapor)

$\Delta = 1.43$ Mol. Wt. = 88.06; $T_c = 523.1$ $\rho_c = 0.3077$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
90	.307	.8065	15.74	15.58	15.04
120	.248	.7580	12.08	12.10	11.73
150	.192	.7005	8.85	8.84	8.56
180	.134	.6265	5.70	5.58	5.57
210	.077	.5232	2.94	2.92	2.82
240	.019	.3278	0.50	0.52	0.52

means of equation (13) are regularly lower than those calculated by means of equation (14) and those observed, particularly for the lower temperatures where the accuracy of the observations is quite certain.

The data of the third and fourth columns were taken from S. Sugden.[1] In the fifth column are given the values calculated by means of equation (13), and in the sixth—the values calculated by means of equation (14) as taken from N. Katayama.[2] Table XIII gives the constants Δ, which are approximately the same for all unassociated substances for both liquid and vapor states. In the second column of this table is also given the constant K of equation (14).

TABLE XIII

The Equation of State for Liquid-Vapor Interfaces

Constants

	Δ	K
Benzene	1.39	2.04
Chlorobenzene	1.39	2.02
Ethyl Ether	1.39	2.04
Carbon Tetrachloride	1.39	2.05
Methyl Formate	1.31	2.15
Ethyl Acetate	1.43	1.97

Summary

1. On the basis of Antonoff's rule and the capillary rise equation of surface tension, an expression is deduced which determines the surface tension of saturated vapors.

2. This expression is further developed into a form which relates surface tension of saturated vapors with temperature. The equation is tested for six unassociated vapors and found to reproduce observed results with fair accuracy.

3. The various modifications of Eötvös' law are discussed, and a new one is developed which takes account of the vapor density and is based on the theory of corresponding states. This new equation is tested against the same six compounds in the liquid state and is found to be in good agreement with observed data.

Chemical Laboratory
Howard University
Washington, D. C.
December 1930.

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[1] Loc. cit.

[2] Loc. cit.

THE INTERACTION BETWEEN NITRIC OXIDE AND HYDROGEN SULPHIDE IN THE PRESENCE OF WATER

BY H. B. DUNNICLIFF, SARDAR MOHAMMAD AND JAI KISHEN

Recently, J. A. Pierce[1] has studied the reaction between nitric oxide and hydrogen sulphide from the thermodynamic point of view. He concludes that "the assumption of Thomson[2] that nitric oxide and hydrogen sulphide react to form ammonium sulphide and nitrous oxide is obviously incorrect: absence of the former by qualitative tests being sufficient indication of this. The counterclaim of Le Conte[3] that the gases do not react at all is likewise refuted." He has established that the gases react together with formation of water, sulphur and nitrogen according to the stoichiometric equation:

$$2NO + 2H_2S = 2H_2O + 2S + N_2,$$

though the mechanism is more complex. The present work communicates a study of the reaction between the two gases in the presence of much water.

The Soluble Products of the Reaction between Nitric Oxide and Hydrogen Sulphide in the Presence of Water

Hydrogen sulphide was prepared from ferrous sulphide and hydrochloric acid and purified by passing it first over dry iodine crystals and then through a dilute solution of sodium sulphide. Nitric oxide was made by dripping a concentrated solution of sodium nitrite into an acidified solution of ferrous sulphate.[3] Nitric oxide and hydrogen were passed into water in a two-litre flask from which air had been displaced by carbon dioxide gas. Milkiness due to sulphur was observed after some time. After a few hours the solution became yellow and more sulphur was formed and deposited. The interaction appeared to take place more rapidly when traces of nitrogen peroxide were previously introduced into the solution. The atmosphere over the solution remained clear throughout the reaction and the brown colour of nitrogen peroxide was never observed inside the flask. The yellow solution immediately became white when it was exposed to the air and some of the sulphur in the solution also seemed to coagulate. Cadmium carbonate was added to remove the excess of hydrogen sulphide and to deposit sulphur. The solution gave tests for 'ammonium' but hydroxylamine was absent. A nitrite was present but no nitrate. Acetic acid, when added to the solution obtained after the passage of the gases through water for several hours, produced a transitory yellow colour which indicated the presence of some sulphur acid. Qualitative tests showed that a thiosulphate was present but tetrathionate and other thionic acids were not detected. This contradicts the result previously announced[4] where it is stated that tetrathionate is present and nitrite is absent. The results given in the present article have been often confirmed.

Quantitative Determination of the Products of Reaction in Solution

'Ammonium.' Sodium hydroxide solution was added in excess to the original solution containing colloidal sulphur. Steam was blown through the solution and the ammonia absorbed in excess of standard sulphuric acid.

Nitrite and thiosulphate were estimated by the following methods. Cadmium carbonate freshly precipitated from a solution of cadmium sulphate by ammonium carbonate was employed to remove the excess of hydrogen sulphide and to deposit sulphur from the solution.

1. (a) Excess of potassium permanganate was added to oxidise completely both thiosulphate and nitrite. Ferrous sulphate was then added in excess and the excess of ferrous sulphate was back titrated against potassium permanganate.[5]

(b). The thiosulphate was estimated by titration against a standard solution of iodine. Control experiments indicated that when the quantity of a nitrite in a mixture of a thiosulphate and a nitrite is not large, the thiosulphate could safely be determined by this method.

2). The nitrite and thiosulphate were exactly oxidised as described above. The nitrite formed as the result of oxidation was determined by the method of Bowman and Scott.[6] The results of three experiments are recorded in Table I. The amount of ammonia was always in excess of that calculated for the nitrite and thiosulphate present, both when Merck's extra pure cadmium carbonate or freshly precipitated and thoroughly washed cadmium carbonate was used. This was found to be due to small quantities of ammonia present in the cadmium carbonate. Hence, the solution which contained colloidal sulphur was used for determining 'ammonium' (V.S.).

The quantities of the products formed in the reaction are small. Errors in estimation were reduced by taking large volumes of the solutions. In the determinations of the nitrite the solution was evaporated to small bulk after oxidation.

TABLE I

The Quantitative Determination of the Products formed in Solution in the Reaction

Composition of the solution in grams per (100 × 10^5) c.c.

Nitrite	Thiosulphate	Total 'ammonium'		Error
		Calculated from Nitrite and Thiosulphate	Determined	%
284	121	150	152	−1.3
376	151	196	191	2.6
527	430	344	349	−1.4

The Gaseous Products of the Reaction

The apparatus for the estimation of nitrogen and nitrous oxide in the gaseous products of the reaction is described in "The Action of Hydrogen Sulphide on Solutions of Nitric Acid."[7] Nitric oxide obtained by the action of sodium nitrite on ferrous sulphate, was passed through a concentrated solution of caustic soda and then over solid caustic soda to purify it from traces of nitrogen peroxide. It was stored in the gas pipette, H_1, (Fig. 1) over water the surface of which was covered with a layer of paroleine. The tower, D, connected with the reaction flask, C, contained cupric phosphate to remove the excess of hydrogen sulphide.[8] Paraffin wax had been run through the rubber tubing used as connections to prevent the action of nitric oxide on the rubber. Before commencing an experiment, the whole apparatus was swept clean of other gases by a stream of carbon dioxide. The two gases were then admitted into the reaction flask, C, which would be easily shaken. The gases were allowed to stand for some hours and the reaction flask was occasionally shaken. When interaction appeared to be complete the gaseous mixture was swept forward through the cock F_1, and a further supply of gases was introduced into C. Any excess of nitric oxide was absorbed in a series of vessels E_1, E_2, (Fig. 1) E_3, (Fig. 2)[7] of different forms each containing a mixture of

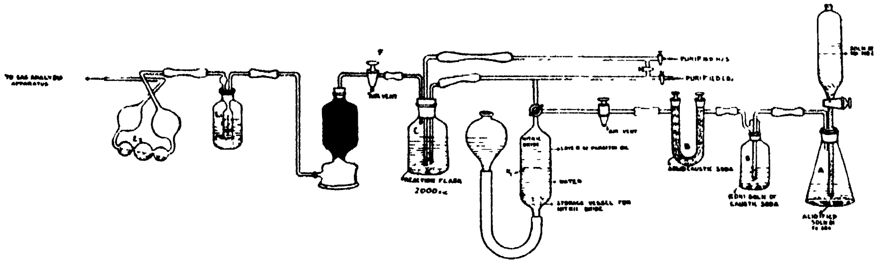


FIG. 1
(Diagrammatic)

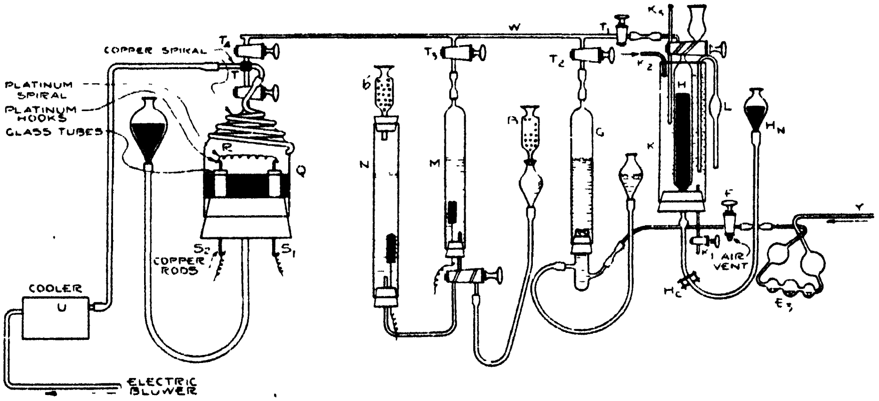


FIG. 2

five volumes of a saturated solution of potassium bichromate with one volume of concentrated sulphuric acid.[9] This mixture oxidises nitric oxide quantitatively to nitric acid and is stable at ordinary temperatures. The residual gases were finally swept out by carbon dioxide and collected over caustic potash in the tube G, Fig. 2,[7] through the cock F. The residual gases (N_2O and N_2) had then to be brought under combustion with excess of hydrogen in the pipette described in Fig. 3.[7] The contraction produced should be equal to the volume of nitrous oxide.

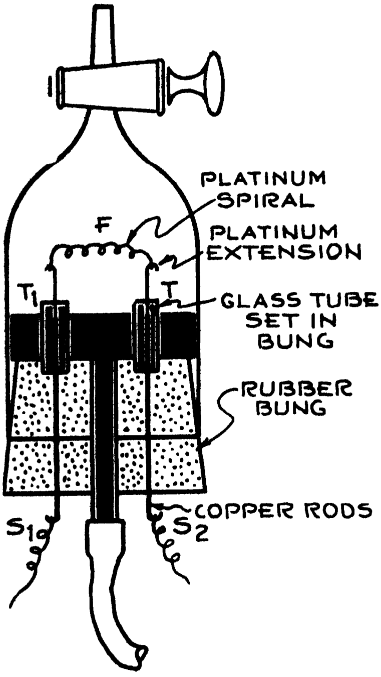


Fig. 3
Combustion Pipette

In Table II (i) and (ii) are given the results of two experiments performed under similar conditions, i.e., the whole of the gases evolved were collected, the analyses being of average samples.

In (ii), the gaseous products from the first two hours' reaction were let out through the air-vent cock F_1. Subsequent quantities of the two gases formed in the reaction were then collected in G.[7] The mixture had the same composition as the gas collected during the first two hours. This shows that the chemical change is the same during those two periods of the reaction.

In order to find out if the gases are in the same proportion in both the gas and liquid phase the gases were collected (a) from the gaseous phase above the liquid and (b) by bubbling carbon dioxide through the liquid.

It was found (vide results Table III, i and i.a) that (a) contained a lower percentage of nitrous oxide than (b) (vide Table III, ii).

This may be due to the fact that nitrous oxide, the first reduction product, is removed from the sphere of action by its relatively high solubility in water or that nitrous oxide is formed in the liquid phase either exclusively or in greater quantity than in the gas phase. This point is under investigation.

Table II

Analysis of the Gaseous Products of the Reaction

	Vol. of the gas c.c.	Vol. of hydrogen c.c.	Vol. after combustion c.c.	Contraction N_2O c.c.	N_2 c.c.	Composition N_2O %	Composition N_2 %
i.	13.6	31.0	42.8	1.8	11.8	13.2	86.8
i. a	24.6	40.2	61.6	3.2	21.4	13.0	87.0
ii.	32.2	43.8	71.9	4.1	28.1	12.7	87.3

TABLE III

The Gaseous Products formed when Hydrogen Sulphide and Nitric Oxide are bubbled through Water

		Vol. of the gas c.c.	Vol. of Hydrogen c.c.	Vol. after combustion c.c.	Contraction c.c.	N_2	Percentage composition N_2O	N_2
i.	a	30.2	39.7	73.2	1.7	28.5	5.6	94.4
i.a		24.1	40.8	63.8	1.1	23.0	4.6	95.4
ii.	b	30.2	41.9	64.6	7.5	22.7	24.8	75.2

The Effect of the Presence of Sulphuric Acid

The reaction in the presence of sulphuric acid is more rapid at first than when sulphuric acid is absent, but it slows down very quickly. The milkiness of the solution did not increase and only traces of ammonia were observed. The percentage composition of the residual gases is shown in Table IV.

TABLE IV

The Gaseous Products (from gas and liquid phase) formed when Nitric Oxide and Hydrogen Sulphide are bubbled through Dilute Sulphuric Acid

	Vol. of the gas. c.c.	Vol. of Hydrogen c.c.	Vol. after combustion c.c.	Contraction c.c.	N_2 c.c.	N_2O %	N_2 %
With 5% H_2SO_4							
i.	30.5	44.1	71.6	3.0	27.5	9.8	90.2
With 10% H_2SO_4							
ii.	15.8	31.6	42.9	4.5	11.3	28.5	71.5

The results indicate the formation of a higher proportion of nitrous oxide when sulphuric acid is present. If the formation of nitrous oxide takes place mainly in the liquid phase, this may be due to the greater solubility of nitric oxide in sulphuric acid than in water.

Since, after long passage of the gases (NO and H_2S) through water, the small amount of nitrite is the same as when the gases are passed for a short interval, it appears that either (a) the nitrite is a minor bye-product, or (b) that nitrite is formed as an intermediate product and systematically decomposed. The presence of sulphuric acid practically prevents the formation of ammonia in the solution. This suggests that such ammonia as is formed is not produced in the gaseous phase (when on shaking it would be found in the sulphuric acid) but in solution. This would confirm the observations of Pierce[1] who finds not only that nitrous oxide is not formed when dry nitric oxide and hydrogen sulphide are mixed, but that ammonia also is not a product of the reaction in the absence of water.

The Action of Nitric Oxide on Ammonium Nitrite and Dilute Solutions of Ammonia

(A) *Products found in the Solution.* Nitric oxide was passed into ammonium nitrite solutions of various concentrations in an atmosphere of hydrogen and the excess of nitric oxide was driven off by bubbling hydrogen through the solution. Nitrate was not detected by the most delicate tests. Titration against standard potassium permanganate showed that the amount of nitrite was unchanged. The solubility of nitric oxide in solutions of ammonium nitrite was also determined in the presence of hydrogen. The value found at 20°C agreed fairly with that given by Lunge for the solubility of nitric oxide in water. (Value determined = 0.0070 gram per 100 c.c., Lunge found 0.0068 grams per 100 c.c. at 20°C).

There was no evidence that any chemical action takes place when nitric oxide is passed into dilute solutions of ammonia in an atmosphere of hydrogen.

The Action of Nitric Oxide on Solutions of Ammonium Sulphide

The existence of a thiosulphate in the solution due to the interaction between nitric oxide and hydrogen sulphide suggests the formation of ammonium poly-sulphide (via ammonium sulphide and sulphur) as an intermediate product in the reaction.

Hydrogen sulphide was passed into a solution of ammonia in the absence of air for some time and then excess of the gas was removed from the solution by bubbling hydrogen through it. A little more ammonium hydroxide was added to tend to produce ammonium sulphide from the hydrosulphide. When nitric oxide had been passed through the colourless solution for about 15 minutes, a yellow colour developed and sulphur was thrown down. This sulphur then gradually decreased in quantity as it dissolved in the solution, ultimately giving it an orange colour. The orange colour in the case of weak solutions (approximately N/200) was removed on passing nitric oxide for about twenty hours. Freshly prepared cadmium carbonate was added to deposit sulphur. The results showed that the polysulphides formed seemed to decompose into thiosulphate or thionic acids and sulphur. Since the amount of thiosulphate found in the solutions was small if cadmium carbonate was added immediately after the reaction, it appears that the thiosulphate is produced via the polysulphide. When nitric oxide was passed into N/33 ammonium sulphide for five hours, the thiosulphate formed was 0.2 gram per litre. The amount of thiosulphate increases considerably if the solution is allowed to stand.

Only traces of nitrite were detected. When an insufficient amount of nitric oxide was kept in contact with a strong solution of ammonium sulphide over mercury for about 48 hours, the nitric oxide was completely absorbed in the solution which readily gave tests for a nitrite. There was no possibility of nitric oxide being in excess and forming nitrous acid via oxygen from the air, as it was completely absorbed in the experiment.

Traces of sulphate were present if nitric oxide was bubbled into very weak solutions for several hours when the polysulphide first formed seemed to decompose completely. This may have been due to decomposition of thiosulphate by hydrolysis

$$(NH_4)_2S_2O_3 + H_2O = (NH_4)_2SO_4 + H_2S$$

(B). *The Gaseous Products.* The experiments could not be performed in the presence of carbon dioxide as the solution was completely decomposed when the apparatus was being washed with carbon dioxide. The percentage of nitrous oxide and nitrogen determined from these experiments (N_2O = 13.0%; N_2 = 87.0%) exactly corresponded with the percentage of these gases from the reaction between nitric oxide and hydrogen sulphide in the early stages (vide Table II). This proved that the gaseous products are not obtained from ammonium sulphide and nitric oxide but probably from nitric oxide and hydrogen sulphide in the gas phase, the hydrogen sulphide being drawn out of the hydrolysed ammonium sulphide solution by carbon dioxide. To overcome the difficulty of providing an inert atmosphere over the solution, another apparatus (Fig. 4) was connected with the apparatus for the gas analysis (Fig. 2). The air from the capillary tube was completely expelled by using the same nitrometer as a pump. Nitric oxide prepared in A, by Thiels's method[3] was admitted into the nitrometer, N. A known volume of a solution of ammonium sulphide was drawn into the nitrometer from the cup, G. The nitrometer was shaken occasionally and, after the desired interval for reaction, the residual gases were driven into the apparatus for gas analysis (Fig. 2) by raising the reservoir of the nitrometer and using a current of carbon dioxide. A mixture of 50 c.cs. of N/33 ammonium sulphide solution with 10 c.c. of ammonium hydroxide of the same strength was exposed to 80 c.c. of nitric oxide. After 19 hours the contraction was 26 c.c. The gas collected over caustic potash was 11 to 12 c.c., the balance (nitric oxide) having been absorbed in the dichromate mixture. The results of two experiments performed under similar conditions are shown in Table V.

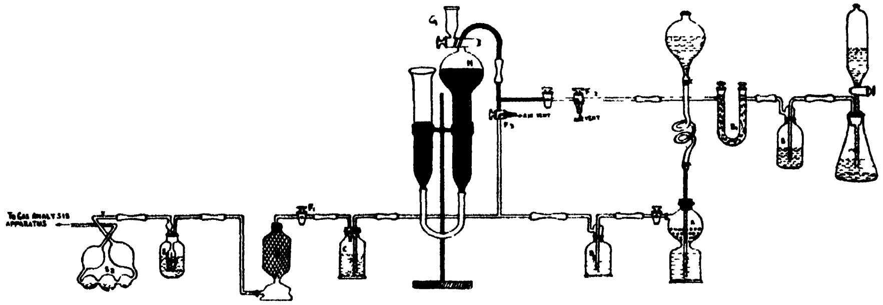


FIG. 4

TABLE V

Analysis of the Gaseous Products of the Reaction between Nitric Oxide and Ammonium Sulphide

	Vol. of the gas c.c.	Vol. of Hydrogen c.c.	Vol. after combustion c.c.	Contraction c.c.	N_2	Composition N_2O %	Composition N_2 %
i.	11.4	18.6	26.8	3.2	8.2	28.1	71.9
ii.	12.0	21.6	30.2	3.4	8.6	28.4	71.6

Nitric oxide was in excess in these experiments.

Experiments were performed in which the excess of the reducing agent i.e., ammonium sulphide, was exposed to nitric oxide. In Table VI are given the results of two experiments carried out under similar conditions in which 82 c.c. of nitric oxide, were allowed to react with 50 c.c. of ammonium sulphide solution (approximately N/10) and 10 c.c. of N/33 ammonium hydroxide. After 19 hours the residual gas, *which was free from nitric oxide,* was about 21 c.c. in the first experiment and 17.2 c.c. in the second experiment.

TABLE VI

Analysis of Residual Gas from the Action of Nitric Oxide with Excess of Ammonium Sulphide

	Vol. of the gas c.c.	Vol. of Hydrogen c.c.	Vol. after combustion c.c.	Contraction c.c.	N_2 % c.c.	N_2O %	N_2 %
i.	21.2	33.4	54.5	0.1	21.1	0.0	100.0
ii.	17.2	31.0	48.2	0.0	17.2	0.0	100.0

These experiments show that when an excess of the reducing agent is used, the gaseous product of the reaction consists of pure nitrogen. The percentage of nitrous oxide is increased by using an excess of the oxidising agent, i.e. nitric oxide. Bancroft[10] from a study of the reduction of nitric acid by metals arrived at the same conclusions: "In the first case there is never an appreciable concentration of the reducing agent, hence its potential is low, and the reduction will not go so far. In the second case there is always an excess of reducing agent and the reduction should go to a lower stage than in the first case. There is a little chance for nitric acid to react with the intermediate products. An excess of reducing agent will cause more complete reduction to a lower stage."

It also shows that nitric oxide is reduced to nitrogen via nitrous oxide under favourable conditions and is conclusive evidence that nitrous oxide is reduced to nitrogen by hydrogen sulphide (or ammonium sulphide).

The Action of Nitric Oxide on Ammonium Thiosulphate

(A). *The Products of the Reaction in Solution.* On passing nitric oxide into solutions of ammonium thiosulphate in an atmosphere of hydrogen, a transitory yellow colour is observed with deposition of sulphur in small quantities. The decomposition of the thiosulphate increases with the decrease in the concentration of the solutions but the amount of ammonia in a solution remains constant. Table VII shows the decomposition of solutions of ammonium thiosulphate of different strengths.

TABLE VII

The Decomposition of Ammonium Thiosulphate by Nitric Oxide

Composition of the solution grams per 100 c.c.

	Strength of the solutions	$(S_2O_3)''$ taken	$(S_2O_3)''$ left	Decomposition	Percentage decomposition
i.	N/6	1.867	1.858	0.009	0.5
ii.a.	N/19.7	0.568	0.540	0.028	4.9
b.	N/19.7	0.568	0.529	0.039	6.9
iii.	N/77.14	0.145	0.119	0.026	17.9

TABLE VIII

Showing the Formation and Decomposition of Nitrite when Nitric Oxide is passed into Mixtures of Ammonium Thiosulphate and Ammonium Nitrite Solutions. The Composition of the Solutions is given in grams per 100 c.c.

	Strength of the solution	Time of passing the gas	Thiosulphate		Decomposition	Percentage decomposition	Nitrite		Increase or Decrease
			Taken	Left			Before the reaction	After the reaction*	
		hours	gram	gram	gram	%	gram	gram	gram
i.	$\frac{N}{23.87}$ $(S_2O_3)''$ $\frac{N}{32.10}$ $(NO_2)'$	1.5	0.469	0.456	0.013	2.8	0.0717	0.0825	+0.0108
ii.	$\frac{N}{24.6}$ $(S_2O_3)''$ $\frac{N}{32.1}$ $(NO_2)'$	1.5	0.456	0.442	0.014	3.1	0.0717	0.0840	+0.0123
iii.	$\frac{N}{18.48}$ $(S_2O_3)''$ $\frac{N}{16.94}$ $(NO_2)'$	4.5	0.606	0.539	0.067	11.1	0.1357	0.0801	−0.0556
iv.	$\frac{N}{49.75}$ $(S_2O_3)''$ $\frac{N}{46.62}$ $(NO_2)'$	4.5	0.225	0.211	0.041	6.2	0.0493	0.0365	−0.0128

* As calculated from permanganate titration. This would show as nitrite any nitric oxide in solution or molecular combination with any compound in solution. The matter is under further investigation.

Sulphate was found to be present in small quantities but tetrathionate was not detected. Nitric oxide was passed into N/20 ammonium thiosulphate solutions for different intervals but the nitrite formed was negligible in all the stages of the reaction. If formed, nitrite is probably decomposed in all stages of the reaction by comparatively strong solutions of ammonium thiosulphate (vide foot-note to Table VIII p. 1729). The transitory yellow colour observed throughout the reaction may be the result of interaction between the nitrite formed and the thiosulphate present.[11] However, an increase in the amount of nitrite was observed (Table VIII) in the early stages of the reaction when nitric oxide was passed into mixtures of equal volumes of ammonium thiosulphate and ammonium nitrite solutions. In the later stages of the reaction, decomposition of nitrite is noticed

When nitric oxide was passed into about N/20 ammonium thiosulphate solutions, sulphate was formed. The results shown in Table IX give the amount of change effected in different intervals of time and it will be observed that there is no regular relationship between the thiosulphate decomposed and the sulphate formed. A small but continuous decrease in the amount of ammonia was observed. The solution was alkaline to litmus after the passage of the gas for nine hours.

TABLE IX

The Amount of Sulphate formed when Nitric Oxide is passed into Ammonium Thiosulphate for different intervals

Quantities are shown in grams per litre.

		1	2	3	4
i.	Time of Passage of Gas (Hours).	1.5	2.5	4.5	9.0
ii.	Thiosulphate taken as $(S_2O_3)''$	5.654	5.654	5.654	5.654
iii.	Thiosulphate left as $(S_2O_3)''$	5.599	5.462	5.101	4.604
iv.	Thiosulphate decomposed as $(S_2O_3)''$	0.055	0.192	0.553	1.050
v.	Sulphate formed as $(SO_4)''$	0.045	0.094	0.297	0.328
vi.	$(NH_4)^{\cdot}$ corresponding to $(SO_4)''$ formed	0.017	0.035	0.111	0.123
vii.	$(NH_4)^{\cdot}$ corresponding to $(S_2O_3)''$ left	1.799	1.756	1.639	1.480
viii.	Total of (v) and (vi)	1.816	1.791	1.750	1.602
ix.	$(NH_4)^{\cdot}$ corresponding to $(S_2O_3)''$ taken	1.818	1.818	1.818	1.818
x.	Percentage. Decrease in $(NH_4)^{\cdot}$		−1.5	−3.7	−11.8

B. *The Gaseous Products of the Reaction.* About 250 c.c. of nitric oxide were kept in contact with 250 c.c. of ammonium thiosulphate solution (about N/50) for twenty hours. The volume of the residual gases collected over caustic potash was small. The results of two experiments are shown in Table X.

TABLE X

Analysis of the Gaseous Products of the Reaction between Nitric Oxide and Ammonium Thiosulphate

	Vol. of the gas. c.c.	Vol. of Hydrogen. c.c.	Vol. after combustion c.c.	Contraction	N_2	Composition	
						N_2O	N_2
i.	12.5	24.1	35.9	0.7	11.8	5.6	94.4
ii.	10.6	18.2	28.2	0.6	10.0	5.7	94.3

The Action of Nitric Oxide on Solutions of Ammonium Tetrathionate

Ammonium tetrathionate was prepared and was estimated by the method of A. Kurtenacker.[12] On passing nitric oxide into solutions of ammonium tetrathionate of various concentrations, a slight turbidity but no coloration was noticeable. The solution became acidic. (Solutions of ammonium tetrathionate become acidic also on long standing). As in the thiosulphate experiments, the total concentration of ammonia in the solution remained unchanged. The solutions did not give tests for a nitrite when the gas was passed for four hours.

TABLE XI

The Decomposition of Ammonium Tetrathionate Solution by Nitric Oxide

Composition of the solution: gram/100 c.c.

	Strength of the solution	Time in hours for passing NO	$(S_4O_6)''$ taken	$(S_4O_6)''$ left	$(S_4O_6)''$ decomposed	Percentage decomposition
i.	N/29.92	1.0	0.869	0.869	0.000	0.0
ii.	N/29.92	2.0	0.869	0.849	0.020	2.3
iii.	N/20.51	4.0	1.091	0.700	0.391	35.9
iv.	N/32.91	4.0	0.680	0.196	0.484	71.2

Nitric oxide was also passed into mixtures of ammonium nitrite and ammonium tetrathionate solutions. The results were comparable with those obtained from mixtures of ammonium thiosulphate and ammonium nitrite solutions. (vide Table XII).

TABLE XII

Shows the Formation and Decomposition of Nitrite when Nitric Oxide is passed into Mixtures of Ammonium Tetrathionate and Ammonium Nitrite Solutions

Composition of the solution: grams per 100 c.c.

	Strength of solutions	Time in hours for NO	$(NO_2)'$ taken	$(NO_2)'$ after the reaction*	Increase or Decrease
i.	$\frac{N}{21.27}$ $(S_4O_6)''$ $\frac{N}{21.94}$ $(NO_2)'$	1.54	0.105	0.127	+0.022
ii.	$\frac{N}{21.27}$ $(S_4O_6)''$ $\frac{N}{21.94}$ $(NO_2)'$	4.0	0.105	0.071	−0.034

* vide footnote to Table VIII, page 1729.

In solution tetrathionates like thiosulphates are not affected by a nitrite in a neutral medium. In the presence of an acid, the solution of a tetrathionate became yellow. For this reason the amount of tetrathionate was not determined in the above experiments as all the methods recommended for the estimation of tetrathionates involve the use of an acid. The production of a transitory yellow colour is not peculiar to thiosulphates in the presence of an acid and a nitrite as stated by Falcoila.[11]

The Action of Hydrogen Sulphide on Nitrous Oxide

It appears from the results given in Tables II, III and IV that nitric oxide can be reduced through nitrous oxide to nitrogen. To confirm this pure nitrous oxide was collected over hydrogen sulphide solutions in the nitrometer N (Fig. 4) in the presence of water. An analysis of the residual gases after 30 hours is given in Table XIII. Quantitative reduction of nitrous oxide to nitrogen was recorded in both experiments.

TABLE XIII

An Analysis of the Gas which results when Nitrous Oxide reacts with Hydrogen Sulphide Solutions

	Vols. of the gas c.c.	Vol. of H_2 c.c.	Vol. after combustion c.c.	N_2 c.c.	N_2 %
i.	20.4	32.4	52.6	20.4	100
ii.	20.0	32.0	52.2	20.4	100

The liquid phase contained sulphur and readily gave tests for ammonia. This reaction is under further investigation.

The Action of Hydrogen Sulphide on Solutions of Ammonium Nitrite

Bagster[13] observed that hydrogen sulphide acts slowly upon ammonium nitrite converting it into ammonia. Small quantities of nitrogen are also evolved when solutions of ammonium nitrite are kept in contact with hydrogen sulphide for a number of days. The residual gases consisted of nitrogen only.

Summary and Discussion

1). Nitric oxide reacts with hydrogen sulphide solution giving ammonium thiosulphate, ammonium nitrite, sulphur, nitrous oxide and nitrogen.

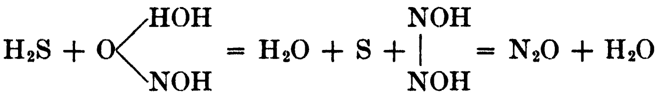
2). Ammonium sulphide solution is decomposed by nitric oxide forming polysulphides of ammonium and small amounts of ammonium thiosulphate and nitrous oxide and nitrogen are evolved. Excess of the reducing agent gives pure nitrogen but excess of the oxidising agent increases the yield of nitrous oxide.

3). Saturated hydrogen sulphide solution completely reduces nitrous oxide to nitrogen and ammonia.

4). Nitric oxide slowly converts dilute solutions of ammonium thiosulphate into ammonium sulphate. Small quantities of nitrogen are formed.

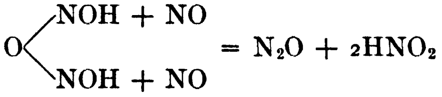
5). Bagster observed that hydrogen sulphide slowly converts ammonium nitrite into ammonia. It has been shown that small amounts of nitrogen are also evolved.

Pierce stated that dry hydrogen sulphide and dry nitric oxide react giving nitrogen and not nitrous oxide. The formation of nitrous oxide is probably due to the water present. Zimmermann[14] observed that aqueous solutions of nitric oxide have a greater conductivity than pure water. He considered that the solution is in part a chemical process giving ionisable substances one of which is possibly Angeli's acid $H_2N_2O_3$ (i. e., $H_2O + 2NO$), derivatives of which are known and which, upon acidification, give nitric oxide. This Angeli's acid may be supposed to react upon hydrogen sulphide.[4]

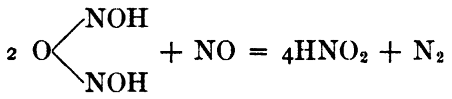


$$H_2S + O\begin{cases} HOH \\ NOH \end{cases} = H_2O + S + \begin{matrix} NOH \\ | \\ NOH \end{matrix} = N_2O + H_2O$$

Previous investigators[15] have found that nitric oxide with water gives not only nitrous acid and nitrous oxide but also nitrogen. Assuming Angeli's acid as an intermediate compound, their formation may be expressed by the equations:[16]



$$O\begin{cases} NOH + NO \\ NOH + NO \end{cases} = N_2O + 2HNO_2$$



$$2\,O\begin{cases} NOH \\ NOH \end{cases} + NO = 4HNO_2 + N_2$$

F. Hefti and W. Schidt[17] found that hydrogen sulphide reacts with nitrous acid to give thiosulphate, sulphur and ammonia. This leads directly to the conclusion that nitrous acid may be the source of all the products obtained by experiment. Bagster has reported the formation of nitrous oxide and nitrogen from the same reaction.

Evidence of the hydration of nitrous oxide to hyponitrous acid is given by Nichols and Derbigney[18] who show a great increase in conductivity of distilled water when nitrous oxide is dissolved in it. The subsequent reduction of the hyponitrous acid by reducing agents probably plays an important part in controlling the amounts of the final products of the reduction of nitric oxide and nitrous oxide:

$$N_2O + H_2O = H_2N_2O_2\text{—reduction}\rightarrow\left[\begin{array}{l} 2H_2O + N_2 \\ 2NH_3 + 2H_2O \end{array}\right.$$

References

[1] Pierce: J. Phys. Chem., **33**, 22 (1929).

[2] Handbuch der anorganische Chemie, **2**, 256 (1907).

[3] I. Thiels: Ann., **253**, 246 (1889).

[4] Dunnicliff and Mohammad: J. Phys. Chem., **33**, 1352 (1929) footnote 3.

[5] Lunge and Smith: J. Chem. Soc. Ind. ii., 465 (1907).

[6] Bowman and Scott: J. Ind. Eng. Chem. **7**, 766 (1915); Cumming and Kaye: "Quantitative Analysis," 84, (1928).

[7] Dunnicliff and Mohammad: loc. cit., pp. 1345 and 1354 (1929).

[8] Harding and Johnson: J. Ind. Eng. Chem. **5**, 836 (1913).

[9] Von Korre: Chem. Ind., **25**, 534 (1902).

[10] Bancroft: J. Phys. Chem., **28**, 744 (1924).

[11] Falcoila: Gazz., **52**, ii, 87 (1922).

[12] Kurtenacker: Z. anorg. Chem., **134**, 256 (1924).

[13] Bagster: J. Chem. Soc., **1928**, 2631.

[14] Zimmermann: Monatshefte, **26**, 277 (1893).

[15] Russell and Lapraik: J. Chem. Soc., **32**, 35 (1877); Cook: Chem. News, **58**, 158 (1888).

[16] E. J. Joss: J. Phys. Chem., **30**, 1271 (1926).

[17] German Pat., D.R.P., 422726 (1923).

[18] Nichols and Derbigny: J. Phys. Chem., **30**, 491 (1926).

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RAMAN EFFECT IN THE ULTRAVIOLET REGION

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The Raman spectra of organic substances have recently been the subject of a large number of investigations. The comprehensive papers of Dadieu and Kohlrausch deserve special mention in this connection. These authors have attempted to correlate Raman lines corresponding to various frequency shifts with the characteristic vibration between the different parts of a molecule. Thus for example a Raman shift of 2900-2950 cm^{-1} is ascribed to the vibration between (C-H) a carbon and a hydrogen atom in an aliphatic compound. The importance of such attempts to find out the frequency of vibration between different parts of a molecule for an accurate elucidation of molecular structure can easily be appreciated.

The investigations have mostly been carried out in the visible region of the spectra and the exciting lines have mostly been the following wavelengths in the spectra of mercury lamp:—4358.3, 4347.5, 4339.2, 4108.1, 4077.8 and 4046.8 Ångstroms. The results are in some cases of doubtful accuracy as regards the exact magnitudes of Raman shifts, because of the want of monochromacy in the exciting radiations. In some recent investigations by the students of Raman an attempt has been made to use monochromatic radiations having wavelengths 4358.3, 4347.5 and 4339.2 Å.U. by circulating a solution of didymium chloride round the liquid under excitation.

In the ultraviolet spectrum from a quartz mercury lamp there are two strong lines 3131.7 and 3125.7 of comparable intensities and the nearest strong lines from these, are 3341.5 Å.U. and 3021.5 Å.U. with a frequency difference of 2000 and 1000 cm^{-1}, approximately. The Raman lines due to the scattering of these two wavelengths by a liquid can be easily picked out because there would be a constant frequency difference of 61.5 cm^{-1}. Hence the Raman shifts produced by a liquid exposed to radiation could be unequivocably determined. Apart from this intrinsic interest in the investigation of Raman effect by ultraviolet light from a mercury lamp, it was hoped that new lines which were too feeble when produced by longer wavelengths might be detected in scattering due to shorter wavelengths. In this paper are described the results of an investigation on Raman radiation in the ultraviolet produced by the following substances, the references referring to work on the Raman spectra in the visible:—

(1) Water,[1] Methyl alcohol.[2]

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[1] Daure: Compt. rend., **186**, 1833 (1928); Rao: Ind. J. Phys., **3**, 123 (1928); Venkateswaren and Karl: Z. Physik, **3**, 123 (1928).

[2] Venkateswaran and Karl: Z. physik. Chem., **B. 1**, 466 (1928); Ganesan and Venkateswaran: Ind. J. Phys., **4**, 195 (1929).

(2) Formic acid, Ethyl formate,[3] Sodium formate, Acetic acid,[4] Ethyl acetate,[5] Sodium acetate,[6] Ethyl benzoate,[7] Benzoic acid, Sodium benzoate, Trichloroacetic acid, Sodium trichloroacetate, Monochloroacetic acid, Sodium monochloroacetate, Malonic acid, Sodium malonate and Ethyl malonate.[8]

Experimental Method

Preparation of pure substances:—It is of importance that the substances to be used should be chemically the purest available. In most cases Merck's extra-pure substances were taken for the purpose and in some cases also Kahlbaum's pure chemicals. They were purified by repeated distillations until they were very clear, free from dust and other fluorescent impurity.

The method of illumination is similar to that advocated by Wood.[9] A quartz tube with two side tubes and flat ends fused into it was used for containing the liquid under investigation. The tube was placed horizontally in front of the slit of the quartz spectrograph and was immersed in water contained in a glass tank with two quartz windows.

The open ends of the side tubes were always above the water level. A horizontal quartz mercury lamp was suspended above the glass tank, as close to the quartz tube as possible. The water in the glass tank was frequently renewed. The slit of the spectroscope was shielded from direct illumination by the quartz lamp by suitable screens and practically the whole of the light that entered the spectrograph was due to scattering at right angles.

The spectrum of the scattered light was photographed with a Hilger E_2 quartz spectrograph using Ilford Isozenith plates (H and D 700). The time of exposure varied from three to five hours for different substances. In order however to obtain the fainter details, exposure of ten to twelve hours was given.

The wavelengths of the lines appearing in the spectrogram were calculated with a Hilger travelling micrometer. Hartmann's simplified interpolation formula $\lambda = \lambda_0 + \frac{c}{n-n_0}$ was used with the neighboring mercury lines as standards of reference. The Raman lines falling on the incident mercury lines are not measured.

Experimental Results

In Table I are given the wavelengths, the corresponding frequencies expressed as wave numbers per cm. in vacuum and the notations of the exciting mercury lines.

Raman spectrum of redistilled water. The Raman spectrum of water has been investigated by a large number of workers in the visible region and is

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[3] Pal and Sen Gupta: Ind. J. Phys., 5, 13 (1930); Dadieu and Kohlrausch: Sitzungsber. Akad. Wiss. Wien., **138**, 41 (1929).

[4] Dadieu and Kohlrausch: loc. cit.; Venkateswaran: Phil. Mag., 7, 597 (1929); Ganesan and Venkateswaran: Ind. J. Phys. 4, 195 (1929).

[5] Dadieu and Kohlrausch: loc. cit.

[6] Dadieu and Kohlrausch: Sitzungsber. Akad. Wiss. Wien., **138**, 635 (1929).

[7] Dadieu and Kohlrausch: Sitzungsber. Akad. Wiss. Wien, **138**, 799 (1929).

[8] Dadieu and Kohlrausch: loc. cit.; Pal and Sen Gupta: Ind. J. Phys., 5, 73 (1930).

[9] Phil. Mag., 6, 729 (1928).

TABLE I

λ in I.A.	4358.34	4347.50	4339.23	4108.08	3077.83
ν in cm.$^{-1}$	22938	22995	23039	24335	24516
Notations	e	f	g	h	i
λ in I.A.	4046.56	3983.96	3906.40	3663.28	3654.83
ν in cm^{-1}	24705	25094	25592	27290	27353
Notations	k	l	m	o	p
λ in I.A.	3650.15	3341.48	3131.7 (mean)	3125.66	3021.50
ν in cm^{-1}	27388	29918	31922	31984	33087
Notations	q	r	s	t	u
λ in I.A.	2967.28	2925.41	2893.60	2803.48	2752.78
ν in cm^{-1}	33691	34173	34549	35660	36316
Notations	v	w	x	y	z
λ in I.A.	2652.04 (group)				
ν in cm^{-1}	37673 (mean)				
Notations	z_1				

characterised by its broad bands. In the ultraviolet region it behaves in a manner very similar to that of the visible region.

The most conspicuous band is the one shifted from the exciting lines 3132 and 3126 by about 3400 wave-number and extends from λ3524.3 to 3479.0. Even on close examination the surface of the band is very difficult to ascertain but however it exhibits more or less well defined edges. The central portion of the band is of maximum intensity and is at a distance of 3444 wave-numbers from the exciting lines.

TABLE II

Methyl alcohol—CH_3OH

Wave No. of the Raman lines (Vac.)	I	Exciting lines and Δν	Wave No. of the Raman lines (Vac)	I	Exciting lines and Δν
28979	2	s-2943	30952	4	t-1032
29042	0	t-2942	31606	2b	x-2943
30143	5d	u-2944	31714	1	x-2835
30255	5	u-2832	32621	0	?
30458	3	s-1464	32708	2	w-1465 (y)
30519	3	t-1465	32814	2	w-1359
30737	5b	t-1247 v-2954	33372	1	z-2944
30858	5vb	v-2833	34732	2vb	z_1-2941
Line corresponding to s merged into 30858			34844	2vb	z_1-2829

Δν 1032 (4); 1247 (0); 1359 (2); 1465 (3); 2832 (5); 2943 (5d).

Another faint band appears from λ3327.76 to λ3287.44, probably excited by the line 2967.3.

Note:—In the tables that follow the abbreviations used are given below—d—diffuse, b—broad, vb—very broad. It appears at first sight strange that a strong Raman line 30952 cm^{-1} produced by t should be unaccompanied by a line due to s. A closer examination will show that the line 30858 is a very broad one and contains in it unresolved a Raman line having frequency difference 1032 cm^{-1} from the s line.

TABLE III

Sodium formate—HCOONa

This substance was studied in a conc. aqueous solution.

Wave No. of the Raman lines (vac)	I	Exciting lines and Δν	Wave No. of the Raman lines (vac)	I	Exciting lines and Δν
21593	3	e-1345	30641	3	t-1343
21886	1	e-1052	30865	1	v-2826
21962	0	e- 976	31725	1	s- 197
30263	1	u-2824	31789	1	t- 195
30579	3	s-1343			

Δν : 196 (1); 976 (0); 1052 (1); 1344 (3); 2825 (1).

TABLE IV

[*]Ethyl formate—$HCOOC_2H_5$

Wave No. of the Raman line (vac)	I	Exciting line and Δν	Wave No. of the Raman line (vac)	I	Exciting line and Δν
21226	3	e-1712	23693	3	k-1012
21483	3	e-1455	23865	4	k- 840
21563	3	e-1375	24150	1	m-1442
		i-2953	24411	1	p-2942 (q)
21737	5	k-2968	30155	1d	u-2932
21775	6	k-2930	30477	0	s-1445
21840	1	e-1098	30542	0	t-1442
21940	1	e- 998	30763	2b	ν-2928
22104	2	e- 834	30926	0	s- 996
22165	1	l-2929 (f)	31085	0	s- 837
22329	1d	e- 609	31150	0	t- 834
22540	0	?	31375	0	u-1712 (t)
22681	1	m-2911	31585	0	x-2964
23259	0	k-1446	31642	0	u-1445
23617	1	k-1088	32677	0	v-1014

Δν : 609 (1d); 836 (4); 997 (1); 1013 (3); 1093 (1); 1375 (3); 1446 (3); 1712 (3); 2932 (6); 2966 (5).

[*] The peculiar characteristic of the liquid is that a strong continuous spectrum appears in the visible and ultraviolet region when it is studied in a quartz tube. In the visible region it almost disappears when the quartz tube is replaced by a glass one. Owing to the presence of this continuous spectrum the faint Raman lines in the ultraviolet region can not be studied.

Formic acid—HCOOH. This liquid has been investigated by various workers in the visible region. Attempts were made to investigate it in the ultraviolet but the experiments were not successful as formic acid decomposes by the ultraviolet rays.

TABLE V

Sodium Acetate—CH_3COO-Na

(concentrated aqueous solution)

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
30510	2	s-1412	30763	2	v-2928
The line with shift 1412 excited by t remains unresolved with the line below.			31002	0	s- 920
30557	2	s-1345	31061	0	t- 923

$\Delta\nu$: 922 (0); 1345 (0); 1412 (2); 2928 (2);

TABLE VI

Ethyl Acetate—$CH_3COOC_2H_5$

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
28990	8	s-2932	30814	2	s-1108
29051	8	t-2933	30874	2	t-1110
30133	4d	u-2954	31070	2	s- 852
30177	3	s-1745	31133	2	t- 851
30240	3	t-1744	31278	3	s- 644
30462	4	s-1460	31339	3	t- 645
30526	4	t-1458	31539	3	s- 383
30704	4	v-2987	31600	3	t- 384
30754	7	v-2937	32698	0	u- 389

$\Delta\nu$: 385(3); 645(3); 852(2); 1109(2), 1459(4); 1745(3); 2934(8); 2954(4d); 2987(4).

Benzoic acid in methyl alcohol. This liquid has been investigated by Dadieu and Kohlrausch[1] in the visible region. Attempts were made to investigate it in the ultraviolet region but without success, as the substance being highly fluorescent absorbs the ultraviolet rays.

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[1] Sitzungsber. Akad. Wiss. Wien., **138**, 799 (1929).

TABLE VII

Acetic acid—CH_3COOH

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
28979	5	s-2943	30747	4	v-2944
29040	5	t-2944	31033	4	s- 889
30145	3	u-2942	31096	4	t- 888
30250	2	s-1672	31300	2	s- 622
30314	2	t-1670	31364	2	t- 620
30486	0	s-1436	31617	2vb	t- 367
					x-2932
Very feeble line, not measurable and may be due to t.			31696	0	t- 288?
			32689	1	v-1002
30646	0	s-1276	32803	2	v- 888

$\Delta\nu$: 288(0); 367(0); 621(1); 888(4); 1002(1); 1276(0); 1436(0); 1671(2); 2943(5).

TABLE VIII

Ethyl Benzoate—$C_6H_5COO\text{-}C_2H_5$

This liquid being highly fluorescent can not be investigated in the ultraviolet region

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
21216	7	e-1722	Here the Raman lines excited by p and 9 with 3075 have fallen on an incident Hg line which has become very broad.		
21336	10	e-1602			
21485	2b	e-1453			
21640	10b	e-1298 (k)			
21729	4b	k-2976 (f)			
21835	3	e-1103			
21939	7	e- 999	25685	5	o-1605
22087	3	e- 851	25748	4	p-1605
22323	3	f- 672	25784	8	q-1604
22609	3	e- 329	26016	4	o-1274
22747	3	e- 191	26078	4	p-1275
23099	6	k-1606	26115	7	q-1273
23484	4	i-1032	26507	3	p- 846
23538	4b	k-1167	26543	3	q- 845
23596	3	k-1109	The Raman line due to o with shift 618 coincides with Hg line		
23696	10	k-1009			
23855	6	k- 850			
24088	5	k- 617	26735	1	p- 618
24215	3	o-3075	26773	3	q- 615

$\Delta\nu$: 191 (3); 329 (3); 617 (5); 672 (3); 848 (6); 1004 (10); 1032 (4); 1106(3); 1167 (4b); 1274 (7); 1298 (10b); 1453 (2b); 1604 (10); 1722 (7); 2976 (4b); 3075 (3).

TABLE IX

Sodium benzoate—C_6H_5-COONa

This substance is studied in a concentrated aqueous solution

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
28855	3	s-3067	30918	4	s-1004
28016	3	t-3068	30981	4	t-1003
30320	6	s-1602	31074	1	s- 848
30382	6	t-1602	31138	1	t- 846
30520	5	s-1402	31304	1	u-1783?
30583	5	t-1401	31484	1	u-1603
30765	2	v-2926			

$\Delta\nu$: 847 (1); 1004 (4); 1402 (5); 1602 (6); 2926 (2); 3068 (3).

TABLE X

Sodium malonate—NaOOC-CH_2-COONa

(Concentrated aqueous solution)

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
30154	0	u-2933	30548	0	s-1374
30301?	00		30675	0	s-1247(t)

$\Delta\nu$: 1374 (0); 1247 (0); 2933 (0).

TABLE XI

*Malonic acid—COOH-CH_2-COOH

(Concentrated aqueous solution)

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
30244	0d	t-1740	31075	0	t- 909
30756	2	v-2935	31353	1	u-1734
31023	0	s- 907	32731	1	v- 960 (u- 356)

$\Delta\nu$: 908 (0); 960 (1); 1737 (1); 2935 (2).

* The faint Raman lines in malonic acid cannot be studied owing to the presence of strong continuous spectrum.

TABLE XII

Ethyl malonate—C_2H_5-COO-CH_2-COO-C_2H_5

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
28984	2vb	?	30533	1	t-1451
30147	0	u-2940	30719	0	v-2972
30469	1	s-1453			

$\Delta\nu$: 1452 (1); 2940 (0); 2972 (0).

Table XIII

*Sodium trichloroacetate—CCl_3COONa (Concentrated aqueous solution)

Wave No. of the Raman lines (vac)	I	Exciting line and Δν	Wave No. of the Raman lines (vac)	I	Exciting line and Δν
22518	4	e- 420	24280	1	k- 425
22658	2	e- 280	31500	1	s- 422
23773	2	i- 743	31563	1	t- 421
23852	1	i- 664			

Δν: 280 (2); 422 (4); 664 (1); 742 (2).

* Trichloroacetic acid, its sodium salt and monochloracetic acid, its sodium salt (Tables XIII-XVI) are all investigated in the visible region with a glass plate in between the mercury lamp and the quartz tube.

Table XIV

Trichloroacetic acid—CCl_3COOH (Concentrated aqueous solution)

Wave No. of the Raman lines (vac)	I	Exciting line and Δν	Wave No. of the Raman lines (vac)	I	Exciting line and Δν
22102	1	e- 836	24275	3	k- 430
22240	1	f- 755	31508	4	s- 414
22508	4	e- 430	31570	4	t- 414
22652	2	e- 286			
		k- 842	31658	2	s- 264
23863	2	i- 653	31721	2	t- 263
24143	1	m-1449			

Δν: 264 (2); 286 (2); 414 (4); 430 (4); 653 (2); 755 (1); 836 (1); 1449 (1).

Table XV

Monochloroacetic acid—$CH_2ClCOOH$ (Concentrated aq. solution)

Wave No. of the Raman lines (vac)	I	Exciting line and Δν	Wave No. of the Raman lines (vac)	I	Exciting line and Δν
21514	0	e-1424	30200	1	s-1722
21745	2	k-2960	30264	1	t-1720
22132	2	e- 806	30500	0	s-1422
23901	1	k- 804(s)	30709	1	v-2982
23992	0	m-1600 (l-1102)	31117	3	s- 805
28960	5	s-2962	31178	3	t- 806
29022	5	t-2962	31490	0	s- 432
30124	2	u-2963	31550	0	t- 434

Δν: 433 (0); 805 (3); 1423 (0); 1600 (0); 1721 (1); 2962 (5); 2982 (1).

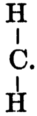
TABLE XVI

Sodium monochloroacetate—$CH_2Cl\text{-}COONa$
(Concentrated aq. solution)

Wave No. of the Raman lines (vac)	I	Exciting line and Δν	Wave No. of the Raman lines (vac)	I	Exciting line and ∇ν
21565	1	i-2951	30133	1d	u-2954
21756	1	k-2949	30518	2	s-1404
22160	0	e- 778	30582	2	t-1402
23782	1	k- 923(i)	31132	1	s- 790
23927	1	k- 778	31193	1	t- 791
28970	2d	s-2952	31681	0	u-1406
29031	2d	t-2953			

Δν: 778 (1); 791 (1); 923 (1); 1404 (2); 2952 (2d).

Discussion of Results

Dadieu and Kohlrausch have ascribed the frequency shifts 2900-3000, 1600-1700, 1350-1450 respectively to the following vibration bonds $-C-H$, $C=O$,  $\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}$. Most of the lines whose frequency shifts are less than 1070 are due to vibration between the radicals forming the molecule. Thus the frequency shifts between 1000-1070 are supposed to be due to the vibration between the CH_3 or OH group against a residual group containing CH_2. The frequency shifts between 700 and 1000 are due to vibration between two parts of an organic molecule at C-C linkage. These suggestions are very interesting but they still lack convincing proof. Some of the results described here do not support in its entirety the hypothesis of Dadieu and Kohlrausch. For example formic acid, sodium formate and sodium benzoate give frequency shifts lying between 1340-1405 though they do not contain a CH_2 linkage. It is very probable that this frequency shift may be also due to a C-(OH) vibration. Again the frequency shifts 1600-1700 are given by all acids containing COOH group, except trichloroacetic acid which is a strong acid. The sodium salts of all the acids studied here do not give the frequency shift 1600-1700 though they all contain the $C=O$ linkage. Only in the case of sodium acetate a very faint line having frequency shift 1649 ($I=00$) have been observed by Dadieu and Kohlrausch. This is most probably due to the presence of a trace of free acetic acid due to hydrolysis. It is clear therefore that the frequency shift 1600-1700 is suppressed when the $C=O$ linkage forms part of a negative ion (the frequency shift 1602 in sodium benzoate is due to the benzene ring.)

Kohlrausch and Dadieu calculate 832 cm^{-1} as the frequency for the vibration C-Cl. Bhagavantam and Venkateswaran found 750 cm^{-1} in the Raman spectra of all organic compounds containing chlorine with the exception of isopropyl chloride. In trichloracetic acid we find both the shifts 836 cm^{-1} and 755 cm^{-1} while in its sodium salt only the frequency shift 743 cm^{-1} is observed. In mono-chloracetic acid we obtain the frequency shift 805 cm^{-1}, but in sodium salt the shift is somewhat less, 778, 791. This diminution in the frequency shifts as we pass from the halogen substituted acids to their sodium salts is rather remarkable.

It is noteworthy that under the influence of ultraviolet rays between 2000 and 3000 Å, formic acid undergoes decomposition, and the halogen substituted acids undergo hydrolysis. We have not been able to observe any Raman shift by scattering of mercury lines of wave-length greater than 3000 Å from these substances, when the exciting light also contained wave-lengths between 2000-3000 Å. If the radiations between 2000-3000 Å from a quartz mercury lamp are removed by the interposition of a glass plate, Raman shifts characteristic of these substances by the scattering of mercury lines of lower wave-lengths are observed. We are therefore led to the conclusion that a molecule cannot produce Raman lines by scattering light of a lower frequency if it is simultaneously exposed to high frequency radiations which are capable of decomposing it. Further investigations on this point are in progress.

Chemical Laboratory,
University of Dacca,
November 15, 1930.

STUDIES ON PHOSPHORIC ACID*

IV. Oxonium Salts of Ortho Phosphoric Acid with Certain Organic Compounds

BY G. BROOKS KING[1] AND JAMES H. WALTON

The purpose of this investigation was to study the formation of oxonium salts of phosphoric acid with various organic compounds, further, to make a comparison of phosphoric and sulfuric acids with regard to their ability to form addition compounds with organic substances.

The present work was suggested by an investigation in this laboratory by Walton and Kepfer[2] in which the solubility of several organic acids in solutions of ortho phosphoric acid was studied. Using solutions of phosphoric acid of various concentrations they found indications of compound formation with the following organic acids: oxalic, succinnic, malic, citric and iso-valeric. The solubility of phenol was also determined and a compound indicated. No attempt was made to determine the composition of these compounds. It was of interest to investigate the formation of these substances by means of a phase rule study of the freezing point curves of mixtures of the pure components.

A phase rule study of phosphoric acid with other compounds is mentioned only a few times in the literature and only one case was found where an organic compound was used as one of the components. Rabinow and Jakubsohn[3] determined the freezing point curves of mixtures of phosphoric acid with ethyl ether and found that two compounds were formed; $(C_2H_5)_2O \cdot 6H_3PO_4$ and $(C_2H_5)_2O \cdot 4H_3PO_4$. However, numerous compounds of phosphoric acid and organic compounds have been isolated by Klages,[4] Allendorf,[5] Raikow[6] and others.

Kendall and Carpenter[7] studied the addition compounds of sulfuric acid with organic substances by means of freezing point curves, with a view of getting some insight into the probable mechanism of various sulfonation reactions. Kendall concluded that the greater the difference in acidic strength between two substances, the greater the tendency for addition compound formation. Kendall regards such addition compounds as true oxonium salts, of the following type:

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*Contribution from the Laboratory of General Chemistry of the University of Wisconsin.

[1] The material presented here is a portion of that to be used by G. B. King in his dissertation to be presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] J. Phys. Chem., **34**, 543 (1930).

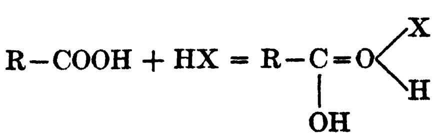
[3] Z. anorg. Chem., **129**, 55 (1923).

[4] Ber., **35**, 2313-2315 (1902).

[5] Ber., **31**, 1298-1301 (1898).

[6] Chem. Ztg., **24**, 367 (1900); **25**, 1134 (1901).

[7] J. Am. Chem. Soc., **36**, 2498 (1914).



$$\mathrm{R-COOH + HX = R-\underset{\underset{\textstyle OH}{|}}{C}=O{<}^{X}_{H}}$$

In the present work a similar study has been made with ortho phosphoric acid and organic substances.

Experimental

Pure ortho phosphoric acid was prepared and dried according to the Ross and Jones[8] method, modified by Walton and Weber.[9] The acid so prepared gave a melting point of 42.5° and 42.6°, taking as the melting point the temperature at which the last crystal disappeared when the temperature was slowly raised. By supercooling some of the fused acid to 40° and then seeding, the acid crystallized and the temperature rose to 42.3°. As this method was used in taking freezing points the above value, 42.3°, was taken as the freezing point of pure ortho phosphoric acid and this value was used in plotting the curves.

Most of the organic compounds used in this investigation were those prepared by Eastman, and in only a few cases was any special purification necessary.

The method of experimentation in the present work is essentially that used by Kendall and his collaborators in their study of freezing point curves. However a freezing point was taken rather than a melting point, as the latter proved unsatisfactory in this work due to the very viscous nature of the phosphoric acid. A Beckmann freezing point apparatus was employed consisting of a 1″ × 8″ hard glass test tube fitted with a rubber stopper, thermometer, stirrer, and a tube for the passage of dry air. A tube with a side arm was employed when the material to be added was a solid. This freezing tube was fitted into a larger test tube which served as a jacket.

Phosphoric acid was weighed out as rapidly as possible in a stoppered weighing bottle and introduced into the freezing tube. Dry air was passed over the mixture in the freezing tube at all times except in the case of benzaldehyde when dry hydrogen was used. The organic substance, if a solid, was introduced into the tube in the form of pills; if a liquid it was weighed out in a weighing pipette and introduced directly into the top of the freezing tube. The solution after being thoroughly stirred was cooled slowly until the solid phase began to separate; in most cases it was necessary, however, to seed the solution. As the solid phase began to separate the temperature rose slightly and the highest temperature was taken as the freezing point of that particular mixture. An approximate freezing point was first run in each case so as to regulate the bath to an appropriate temperature. Freezing points taken by this method must necessarily be slightly low because of supercooling.

Because supercooling was very marked experimental difficulties were very great in the examination of these systems especially near the eutectic on the phosphoric acid side of the system; moreover the mixture would sometimes solidify to a jelly-like mass with no definite point of fusion and it was necessary to remelt and repeat the operation until crystallization took place. This latter difficulty was encountered when supercooling was most marked. In some systems where the freezing point of the mixture was low the phosphoric acid became very viscous and stirring produced minute air bubbles which rendered the solution turbid, making it impossible to detect the formation of minute crystals. In such cases the solution was seeded, cooled, and the lag in temperature, which was always followed by a slight rise, carefully noted. This gave a means of obtaining freezing points in the region of the eutectic with a fair degree of accuracy. As the percentage of phosphoric acid was decreased the freezing point was more definite after the eutectic was passed and the supercooling less marked. Points in the region of the maxima on all curves were very definite but the points in the region of the eutectic are not accurate to more than a degree. In some cases the solutions became so deeply colored that an examination was impossible. If a compound with a congruent melting point is formed in a two component system, a maximum appears in the curve, and from this maximum the melting point and composition of the compound can be obtained.

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[8] J. Am. Chem. Soc., 47, 2165 (1925).

[9] Unpublished results.

Tabulation of Results

I. ACIDS.

1. *Acetic acid:* the compound $CH_3COOH \cdot H_3PO_4$ was obtained; stable at its maximum; melting point 33.8°. The compound is white and crystallizes very readily. Some of the crystals were separated from the mixture and gave a melting point slightly lower than the one recorded above. See Fig. 1, Curve II.

Solid phase H_3PO_4

% H_3PO_4	100	90.8	85.9	84.9
F. T.*	42.3	27.0	14.8	14.0

*Freezing temperature.

Solid phase $CH_3COOH . H_3PO_4$

% H_3PO_4	80.0	77.4	74.8	73.1	72.5	67.5	64.4
F. T.	18.9	21.7	25.6	27.9	29.6	32.7	32.7
% H_3PO_4	63.6	57.4	56.7	51.0	42.6	38.0	
F. T.	33.8	31.6	32.7	30.3	23.0	14.5	

2. *Propionic acid:* no compound was indicated in this system in the region studied. The runs were not carried below −3°.

Solid phase H_3PO_4

% H_3PO_4	100	90.6	84.5	82.4	78.1	74.6	73.0	70.4
F. T.	42.3	33.2	26.3	20.3	12.7	6.2	2.0	−2.(±1°)

3. *n-Butyric acid:* no compound was indicated in the region studied.

Solid phase H_3PO_4

% H_3PO_4	100	87.7	77.8	70.0
F. T.	42.3	34.2	25.8	16.5

On adding more butyric acid the mixture froze around 0° solidifying to a jelly without any definite point of fusion. The runs were discontinued at this point.

4. *n-Caproic acid:* no compound was found in this system. A mixture of the two components was light brown in color.

Solid phase H_3PO_4

% H_3PO_4	93.8	88.6	80.0	72.5	66.4	61.5	56.7	53.9
F. T.	40.9	39.9	38.2	35.8	32.8	30.4	23(±1°)	24.0

5. *Benzoic acid:* no compound was obtained from this system. After the addition of about fifteen per cent benzoic acid, separation into two layers took place and the temperature of fusion remained constant. Also the acid sublimed so readily that any degree of accuracy was impossible.

Solid phase C_6H_5COOH

% H_3PO_4	99.1	98.1	97.1	96.3	95.4	94.3	92.6	90.0
F. T.	44.0	73.0	84.5	92.7	98.0	101.3	106.0	112.0
% H_3PO_4	87.2	84.9	82.6	20.5	17.2	15.4	6.0	0.0
F. T.	113.8	115.5	115.8	116.4	116.5	116.9	119.0	122.3

6. *Pyruvic acid:* the compound $CH_3COCOOH \cdot H_3PO_4$ was obtained; stable at its maximum; melting point 36.4°. Fig. 1, Curve III.

Solid phase H_3PO_4

% H_3PO_4	100	87.6	82.9	77.1
F. T.	42.3	28.0	21.5	16.6

Solid phase $CH_3COCOOH \cdot H_3PO_4$

% H_3PO_4	70.4	69.1	62.7	61.7	54.3
F. T.	24.(±1°)	26.4	33.6	34.4	36.4
% H_3PO_4	52.9	45.7	38.9	30.0	24.3
F. T.	35.8	35.2	33.7	30.6	26.5

7. Several other acids were used as one component with phosphoric acid. Succinnic acid decomposes slowly when heated with phosphoric acid as is evidenced by a slow effervescence. Tartaric acid deepens to a dark brown color with phosphoric acid. Cinnamic acid reacts vigorously with decomposition. o-Toluic acid is insoluble in phosphoric acid. Oxalic acid decomposes rapidly when heated with phosphoric acid. Malic acid is also decomposed readily.

8. *Monochloro-acetic acid:* no compound was indicated in this system. Fig. 1, Curve IV.

Solid phase H_3PO_4

% H_3PO_4	100	96.0	86.5	76.9
F. T.	42.3	38.8	32.1	26.6

Solid phase $CH_2ClCOOH$

% H_3PO_4	66.0	61.5	60.0	58.2	54.0	51.6	46.4
F. T.	38.4	41.1	43.4	44.3	46.6	47.4	49.7
% H_3PO_4	43.4	43.2	35.3	31.6	26.0		
F. T.	50.8	50.6	52.2	54.2	55.0		

9. *Phenylacetic acid:* no compound with phosphoric acid was indicated in a phase rule study of this system.

Solid phase $C_6H_5CH_2COOH$

% H_3PO_4	87.0	79.0	68.1	64.9	60.0	53.0	44.7	27.8
F. T.	45.1	50.7	56.2	58.1	60.0	62.0	64.2	68.3
% H_3PO_4	17.3	9.6	0.0					
F. T.	70.2	72.0	76.7					

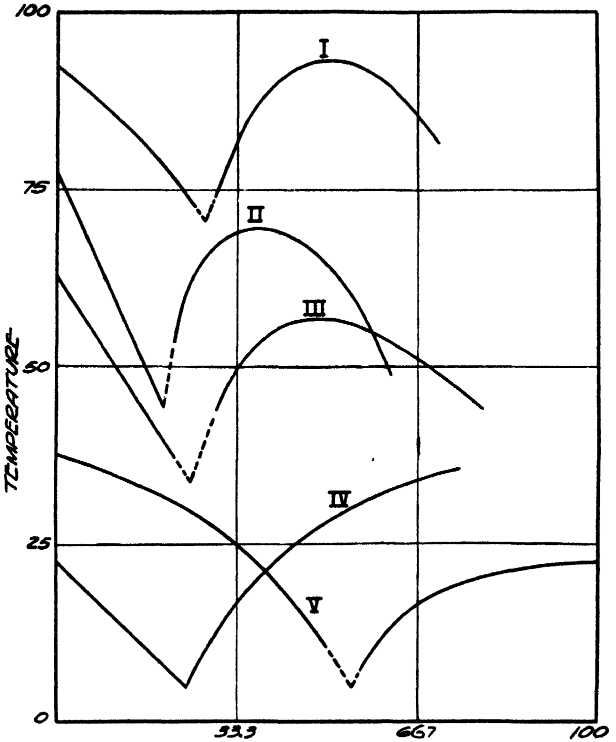

FIG. 1

I. Benzaldehyde and H_3PO_4. Subtract 50 from temp. scale.
II. Acetic acid and H_3PO_4. Subtract 35 from temp. scale.
III. Pyruvic acid and H_3PO_4. Subtract 20 from temp. scale.
IV. Monochloracetic acid and H_3PO_4. Add 20 to temp. scale.
V. Guaiacol and H_3PO_4. Add 5 to temperature scale.

II. ALDEHYDES.

1. *Benzaldehyde:* the compound $C_6H_5CHO \cdot H_3PO_4$ was obtained; stable at its maximum. Melting point 43.0°. The solution of the two components was a light orange in color. Dry hydrogen was passed through the freezing tube at all times to prevent oxidation of the aldehyde. Crystallization was brought about with some difficulty, it being necessary to first freeze the mixture and then preserve a crystal in the upper part of the tube for later crystallization. The freezing point of a mixture which was allowed to stand over

several days varied from that of the original, indicating a probable condensation. Raikow[6] reports the isolation of this compound. Fig. 1, Curve I.

Solid phase H_3PO_4

% H_3PO_4	100	86.0	83.8	76.5	76.0
F. T.	42.3	34.2	32.0	24.9	23.7

Solid phase $C_6H_5CHO \cdot H_3PO_4$

% H_3PO_4	71.3	66.2	65.4	62.5	55.5	54.9	48.0	47.4
F. T.	24.0	31.4	33.6	36.0	40.7	42.6	43.0	42.2
% H_3PO_4	44.7	40.8	35.0	30.7				
F. T.	42.0	40.2	36.3	34.1				

2. *Furfural* which had been freshly distilled, when added to phosphoric acid turned a very dark red, almost black color, rendering an examination of this system impossible.

3. *Anisaldehyde:* the compound $CH_3OC_6H_4CHO \cdot H_3PO_4$ was obtained, stable at its maximum; melting point 83.6°. The mixture of the two components gave a red colored solution.

Solid phase H_3PO_4

% H_3PO_4	100	92.3	90.5	84.7
F. T.	42.3	36.7	34.5	27.5

Solid phase $CH_3OC_6H_4CHO \cdot H_3PO_4$

% H_3PO_4	80.0	77.0	76.0	74.0	72.9	68.0	66.	
F. T.	26(±1°)	40.3	47.6	52(±1°)	52.6	58(±2°)	63(±1°)	
% H_3PO_4	59.2	56.1	52.0	49.5	46.1	43.6	40.0	39.0
F. T.	71(±1°)	74.8	80.5	81.7	83.4	83.4	83.6	83.2
% H_3PO_4	33.0	32.5	30.0	22.0	17.6			
F. T.	81.2	81.5	80.9	76.9	73.7			

III. KETONES.

1. *Benzalacetone:* an examination of this system was impossible as the two components gave a solution almost black in color.

2. *Acetophenone:* the compound $C_6H_5COCH_3 \cdot H_3PO_4$ was obtained; stable at its maximum; melting point 87.9°. Considerable difficulty was encountered on the phosphoric acid side, due to the fact that the solution became a deep green in color and it was difficult to obtain an accurate freezing point. The portion of the curve on the phosphoric acid side before the eutectic was reached is at best only approximate. Klages[4] and Allendorf[5] report the isolation of this addition compound. Fig. 2, Curve I.

Solid phase H_3PO_4

% H_3PO_4	100	99.2	95.8	92.8
F. T.	42.3	40.6	39.0	37.5

Solid phase $C_6H_5COCH_3 \cdot H_3PO_4$

% H_3PO_4	92.5	83.6	76.0	64.4	60.0	55.9	52.3	46.3	41.1
F. T.	36.9	44.8	55.7	73.0	79.3	81.5	87.3	87.9	87.8
% H_3PO_4	33.1	30.0	28.4	22.1	17.6	12.3	3.9	2.4	1.9
F. T.	85.2	83.8	83.5	80.1	77.9	74.5	56.9	52.9	18.7

Solid phase $C_6H_5COCH_3$

% H_3PO_4	0.0
F. T.	18.3

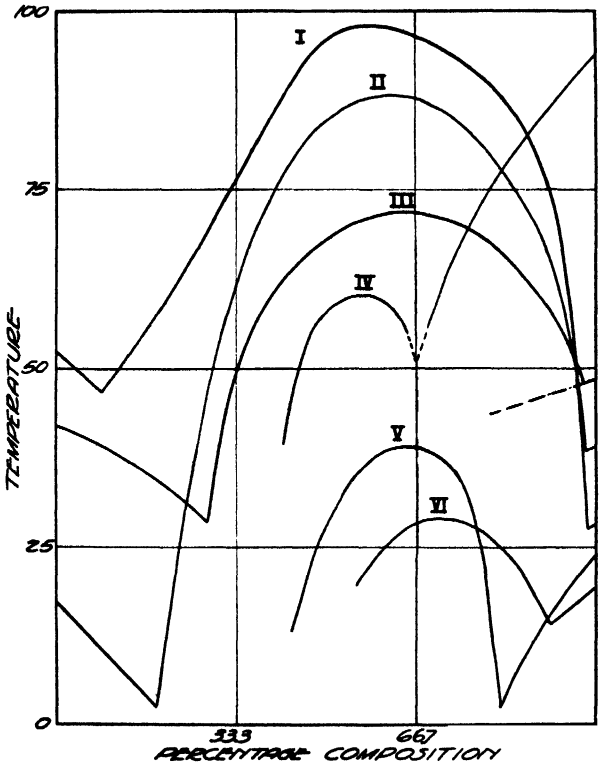

FIG. 2

I. Acetophenone and H_3PO_4. Subtract 10 from temp. scale.
II. Coumarin and H_3PO_4. Add 25 to temperature scale.
III. Benzophenone and H_3PO_4.
IV. *Coumarin and H_2SO_4. Subtract 25 from temp. scale.
V. *Benzophenone and H_2SO_4. Add 25 to temp. scale.
VI. *Acetophenone and H_2SO_4.

* Taken from data of Kendall: J. Am. Chem. Soc., **36**, 2498 (1914).

3. *Benzophenone:* the compound $C_6H_5COC_6H_5 \cdot H_3PO_4$ was found; melting point 71.3°. It was possible to cool below the eutectic of the compound with benzophenone, indicating a metastable state. Fig. 2, Curve III.

Solid phase H_3PO_4

% H_3PO_4	100.	97.6	95.3	93.6	91.5	89.3	88.0	86.0
F. T.	42.3	39.5	39.0	38.5	37.9	37.5	36.7	36.3

% H_3PO_4	84.2	82.3	79.5	76.9	74.3	71.3
F. T.	35.8	34.9	32.9	32.5	30.1	28.5

Solid phase $C_6H_5COC_6H_5{\cdot}H_3PO_4$

% H_3PO_4	65.9	64.7	63.4	59.6	56.3	52.4	49.4	46.6
F. T.	59.1	57.7	61.0	62.9	64.4	66.1	67.4	68.8

% H_3PO_4	44.2	43.0	40.0	37.0	35.6	32.5	33.0	30.6
F. T.	68.9	70.2	70.9	71.3	71.3	71.0	71.2	70.8

% H_3PO_4	28.0	27.9	24.3	24.1	21.3	21.1	18.1	18.1
F. T.	70.4	70.4	69.6	70.2	69.1	69.0	67.8	66.5

% H_3PO_4	16.3	12.6	9.8	4.1
F. T.	67.0	65.9	63.4	58.6

Solid phase $C_6H_5COC_6H_5$

% H_3PO_4	*18.1	*14.2	*6.8	1.7	1.6	0.0
F. T.	43.8	45.4	46.9	47.9	47.8	48.0

* Metastable state.

IV. PHENOLS.

1. *Phenol:* Hoogewerff and van Dorf[10] report the isolation of the compound $C_6H_5OH{\cdot}H_3PO_4$. From the freezing point curve of the components the composition of the compound can not be determined because of the flatness of the curve, indicating a high degree of dissociation of the compound into its components.

Solid phase $C_6H_5OH{\cdot}H_3PO_4$

% H_3PO_4	93.4	81.1	73.1	63.5	55.7	45.	36.5
F. T.	67.5	70.2	70.3	70.3	70.3	69.9	69.4

2. *Guaiacol:* no compound was indicated in the study of this system. Good checks on freezing temperatures could not be obtained at the lower temperatures; the solution was very viscous and crystallization slow. Fig. 1, Curve V.

Solid phase H_3PO_4

% H_3PO_4	100	81.1	73.8	68.0	58.7	51.5	
F. T.	42.3	37.0	34.3	31.3	24.1	15.5	
% H_3PO_4	44.9	34.6	25.4	15.8	9.0	4.0	0.0
F. T.	12(±1°)	20.9	24.5	26.5	26.9	27.3	27.5

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[10] Rec. Trav. chim., 21, 349 (1902).

3. Other phenols: p-cresol, naphthol, thymol, p-nitro-phenol were almost completely insoluble in pure phosphoric acid. Although resorcinol was soluble in phosphoric acid, the solution colored so deeply that no examination was made.

V. ANHYDRIDES.

1. *Benzoic anhydride:* the components in this system were only partly miscible. No compound was indicated in the region which could be investigated.

2. *Coumarin:* the compound $C_9H_6O_2{\cdot}H_3PO_4$ was obtained; stable at its maximum; melting point 113.4°. Fig. 2, Curve II.

Solid phase H_3PO_4

% H_3PO_4	98.8	96.3	93.8	93.0	90.7	88.8	87.1	84.4	82.2
F. T.	39.8	37.1	35.0	33.7	32.3	30.9	29.3	26.6	27.7

Solid phase $C_9H_6O_2{\cdot}H_3PO_4$

% H_3PO_4	80.0	78.4	76.2	68.8	62.8	56.5	50.5	46.5
F. T.	40.8	54.8	63.7	84.6	95.9	104.9	109.7	111.8
% H_3PO_4	40.1	39.5	33.1	30.6	28.1	26.1	22.8	14.4
F. T.	113.4	112.5	111.6	109.0	108.1	107.1	105.0	99.7
% H_3PO_4	11.8	9.2	4.7	2.4				
F. T.	97.7	93.8	86.0	73.3				

Solid phase $C_9H_6O_2$

% H_3PO_4	1.7	1.0	0.0
F. T.	67.9	68.1	68.8

VI. ESTERS.

1. *Methyl Salicylate* and *Phenyl Benzoate* are insoluble in phosphoric acid.

Discussion

The nature of the addition compounds of ortho phosphoric acid with organic compounds is probably that of true oxonium salts. The general rule of Kendall which states that compounds are readily formed from two components of widely different acidic strengths seems to be borne out in the present study. The fact that all the addition compounds contained equimolar quantities of the components indicates that the primary dissociation of phosphoric acid is monobasic, that is

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$$

The dissociation constants of phosphoric acid are given by Abbott and Bray[11] as follows:

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[11] J. Am. Chem. Soc., **31**, 729 (1909).

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_1 = 1.1 \times 10^{-2}$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--} \qquad K_2 = 1.96 \times 10^{-7}$$
$$HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---} \qquad K_3 = 3.5 \times 10^{-13}$$

It is evident from the above that the first acid is much stronger than the other two. Therefore the tendency for compound formation is greatest between the first acid and the organic compound in question. The latter two acids are too weakly acidic to form addition compounds with organic compounds as evidenced by the results in this paper.

Further confirmation of Kendall's rule is evident when we consider the strength of the organic acids used. Acetic acid is a very weak acid, having a dissociation constant of .0000180 as given by Ostwald,[12] and it readily forms a compound with the much stronger phosphoric acid. Likewise with pyruvic acid. Propionic and butyric acids are slightly weaker than acetic acid and would therefore be expected to form similar addition compounds. Because of the necessity of using low temperatures in the study of these acids, thus resulting in very viscous solutions, only a part of the system of each acid was studied. No compounds were indicated in the regions studied. Although addition compounds would be expected, it may be that because of the nearer approach of the organic acid to a hydrocarbon, the influence of the carbonyl group towards acids may be affected in such a manner that no reaction takes place. Monochloro-acetic acid, which has an ionization constant of .00155 does not form an addition compound. Since it is much stronger than acetic acid, the tendency of compound formation should be less. Phenylacetic acid, which is also more acidic than acetic acid does not form a compound with phosphoric acid.

Phosphoric acid has been compared with sulfuric acid with regard to the ability to form addition compounds with organic substances. The results for sulfuric acid are taken from Kendall's data. The curves for the two inorganic acids with the same organic compound are given in Fig. 2. It is to be noted that in all cases the phosphoric acid compounds have a much greater range of stability than the corresponding compound with sulfuric acid. The compounds with sulfuric acid are much less dissociated at the maximum as is evidenced from the sharp breaks in the curves. Both sulfuric and phosphoric acids form equimolecular compounds with coumarin and benzophenone. While acetophenone forms the compound $C_6H_5COCH_3 \cdot H_3PO_4$ with phosphoric acid, it forms the compound $2C_6H_5COCH \cdot H_2SO_4$ with sulfuric acid.

The ability of phosphoric acid to form addition compounds with organic substances seems to be much less than the ability of sulfuric acid to combine with the same compounds. This is readily explainable on the basis of Kendall's rule of acidity, as sulfuric acid is a much stronger acid than phosphoric acid.

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[12] Z. physik. Chem., 3, 418 (1889).

Summary

1. In a series of freezing point determinations, thirty-one organic substances, including acids, esters, aldehydes, ketones, phenols, and acid anhydrides have been investigated with ortho phosphoric acid as one component.

2. Eight addition compounds have been found to exist with the above compounds, their general formula being $=C=O \cdot H_3PO_4$.

3. Kendall's rule of acidity holds in all systems examined.

4. Phosphoric acid forms addition compounds less readily with organic compounds than does sulfuric acid.

5. A comparison of the freezing point curves of the two acids has been made.

Madison, Wisconsin.

THE SOLUBILITY OF NAPHTHALENE IN SOME DERIVATIVES OF FURFURAL*

ARTHUR A. SUNIER

Of late years several investigators[1] have expressed the view that polarity and internal pressure effects were largely responsible for deviations from Raoult's law; and quite recently Sidgwick[2] has emphasized that solubility data often throw considerable light on the nature of the bond in chemical compounds; in particular, such data assist in distinguishing between polar and non-polar bonds.

Naphthalene is believed to be a non-polar compound; it can be readily prepared in a high state of purity; its melting point is rather low, and its latent heat of fusion is known with a fair degree of certainty. Considerations such as these have led several investigators to determine the solubility of naphthalene in a rather large number of solvents. Thus far, however, no determinations have been recorded for derivatives of furfural, no doubt because such compounds have only lately become commercially available. Since furfural is a ring compound containing double bonds and oxygen in the ring it was felt that solubility studies of some of its derivatives might prove of general interest in connection with the general subject of valence mentioned above, as well as of interest to anyone working more directly with these compounds. In the present paper the solvents used were furfuryl alcohol, furfuryl acetate and methyl, ethyl, n-propyl, n-butyl furoates.

Experimental

The synthetic method of Alexejew[3] was employed in making the solubility determinations recorded in the paper. The method consists in heating a sealed tube containing weighed quantities of solvent and solute and noting the highest temperature at which but few small crystals of solute remain in equilibrium with the solution. Ward[4] has described precautions which must be taken to assure the attainment of equilibrium conditions at the solubility temperature. The whole matter has been studied rather thoroughly in this laboratory; the results of this study are to be found elsewhere.[5] The apparatus and procedure were essentially those of Sunier and Rosenblum[6]

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* Contribution from the Chemical Laboratory of the University of Rochester.

[1] Hildebrand: "Solubility" (1924); Proc. Nat. Acad. Sci., **13**, 267 (1927); J. Am. Chem. Soc., **51**, 66 (1929); Ward: J. Phys. Chem., **30**, 1316 (1926).

[2] Sidgwick: "The Electronic Theory of Valency" (1928).

[3] Alexejew: Wied. Ann., **28**, 305 (1886).

[4] Ward: J. Phys. Chem., **30**, 1316 (1926).

[5] Sunier: J. Phys. Chem., **34**, 2582 (1930).

[6] Sunier and Rosenblum: J. Phys. Chem., **32**, 1049 (1928).

which in turn are only slight modifications of the apparatus and procedure used by Ward. In the present research four units were built in close proximity to one another and all stirred and shaken from one motor; it was therefore possible to make four determinations at once. In two of the units were placed bi-metallic thermo-regulators, capable of keeping the two four liter baths to 0.01°; these regulators could be easily adjusted at the end of an hour or half hour period to the next tenth degree (the procedure adopted by Sunier and Rosenblum); this facilitated matters considerably. A two-unit outfit possessing certain advantages is described and discussed in another paper.[1]

The tubes were made up in much the same way as described earlier. With the solvent furfuryl alcohol a slight momentary flash was noted on sealing tubes containing considerable quantities of liquid; this did not, however, cause a loss in weight of more than two milligrams.

The thermometers used were compared, before and after most of the runs were completed, with thermometers recently standardized by the Bureau of Standards.

Materials

All materials were obtained from the Eastman Kodak Company and were their best grades.

The naphthalene was recrystallized from methyl alcohol and care was taken[2] to remove adsorbed solvent from the crystals. The melting point of the recrystallized material was 80.12° when determined carefully in the manner recommended by the Bureau of Standards[3].

None of the solvents was purified further. It would seem desirable to give the physical constants supplied by the manufacturers at the time the materials were purchased:

Furfuryl	Alcholol	B. P.	75– 76° / 17 mm.
"	Acetate	"	84– 85° / 25 mm.
Methyl	Furoate	"	83– 84° / 25 mm.
Ethyl	"	M. P.	30– 33°
n-Propyl	"	B. P.	105–107° / 25 mm.
n-Butyl	"	"	118–120° / 25 mm.

Results

The experimental results are given in Table I. The weight of solute is given first, then the weight of solvent, then the calculated mol fraction and finally the solubility temperature in degrees centigrade.

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[1] Sunier: J. Phys. Chem., **34**, 2582 (1930).

[2] Sunier: J. Phys. Chem., **34**, 2582 (1930).

[3] Bureau of Standards, Sci. Paper No. 340.

TABLE I

Weight $C_{10}H_8$	Weight Solvent	Mol Fraction	Solub. Temp.
Solvent: Furfuryl Alcohol			
1.486	0.4045	0.738	71.4
1.639	0.344	0.785	72.6
1.309	0.617	0.619	68.3
1.011	0.606	0.561	67.2
0.862	0.792	0.455	64.3
0.712	1.649	0.249	53.0
0.826	1.273	0.332	58.7
0.643	2.159	0.186	46.3
0.4667	2.910	0.1094	32.4
Solvent: Furfuryl Acetate			
1.638	0.404	0.816	70.0
1.261	0.703	0.662	61.4
0.941	0.732	0.584	56.2
0.712	0.870	0.472	48.3
1.076	0.438	0.729	65.2
0.541	0.922	0.378	40.9
0.746	0.935	0.466	48.3
0.660	0.925	0.438	46.2
0.798	1.688	0.341	37.4
0.4226	1.902	0.196	19.4
Solvent: Methyl Furoate			
1.462	0.992	0.592	56.8
1.854	0.515	0.780	67.9
1.119	1.035	0.516	51.8
0.887	1.355	0.392	42.3
0.765	1.652	0.313	35.0
0.647	1.927	0.2484	27.7
Solvent: Ethyl Furoate			
1.340	0.423	0.776	66.8
1.177	0.495	0.723	63.5
1.150	0.825	0.604	55.5
1.039	1.280	0.470	44.9
0.812	1.624	0.353	33.8
0.452	1.223	0.288	25.6

TABLE I (Continued)

Solvent: n-Propyl Furoate

Weight $C_{10}H_8$	Weight Solvent	Mol Fraction	Solub. Temp.
1.656	0.525	0.791	67.9
1.201	0.698	0.674	60.1
1.027	1.035	0.544	50.2
1.059	1.376	0.481	45.3
0.953	1.772	0.393	36.4
0.684	1.895	0.303	25.6

Solvent: n-Butyl Furoate

Weight $C_{10}H_8$	Weight Solvent	Mol Fraction	Solub. Temp.
1.234	0.530	0.754	64.9
1.134	0.934	0.615	54.9
1.264	1.514	0.523	47.7
1.093	1.873	0.434	39.2
0.587	1.241	0.383	33.9
0.541	1.810	0.232	21.3

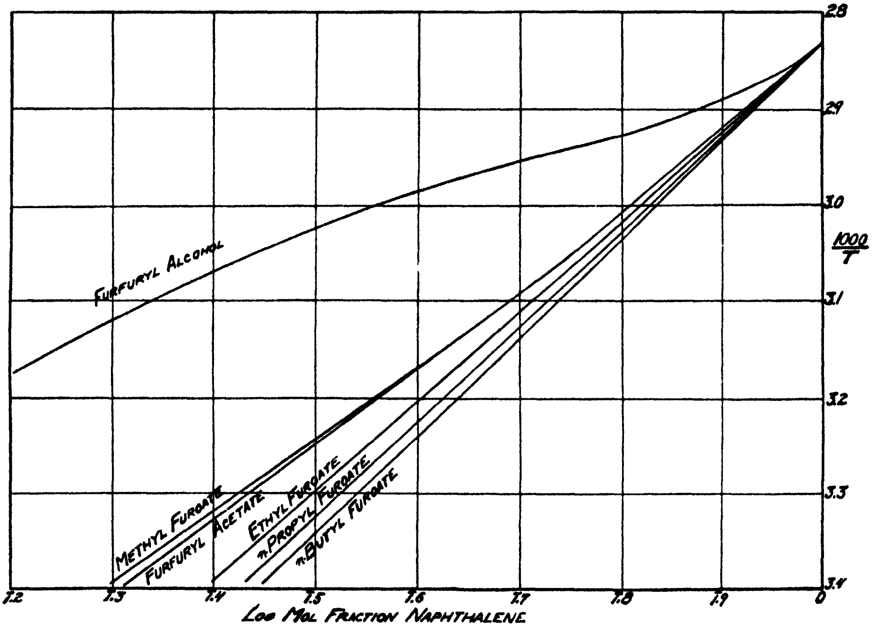

FIG. 1

The results have been plotted in Fig. 1 in the customary way—log N vs 1/T. Large plots were constructed and the mol fractions at rounded temperatures were read off; these values are found in Table II.

TABLE II

Solubility of Naphthalene in Derivatives of Furfural at Rounded Temperatures, expressed in Mol Fractions of Naphthalene

Temp.	Furfuryl Alcohol	Furfuryl Acetate	Methyl Furoate	Ethyl Furoate	n-Propyl Furoate	n-Butyl Furoate
75	0.857	0.900	0.900	0.908	0.910	0.913
70	0.684	0.811	0.811	0.824	0.826	0.830
65	0.474	0.726	0.726	0.747	0.750	0.753
60	0.352	0.644	0.644	0.668	0.678	0.684
55	0.275	0.565	0.565	0.597	0.607	0.618
50	0.219	0.491	0.491	0.531	0.543	0.555
45	0.1758	0.425	0.425	0.471	0.483	0.498
40	0.1446	0.367	0.366	0.415	0.430	0.445
35	0.1194	0.316	0.313	0.365	0.379	0.379
30	0.1048	0.272	0.267	0.321	0.338	0.351
25	0.0849	0.233	0.227	0.281	0.297	0.309
20	0.0728	0.199	0.192	0.246	0.260	0.272

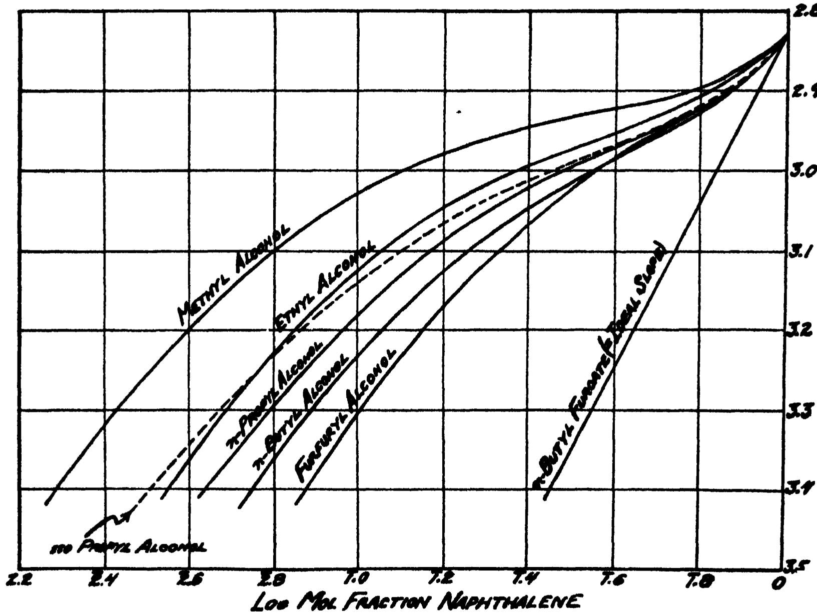

FIG. 2

Discussion of Results

As has been mentioned earlier no recorded data could be found in the literature bearing on these systems; comparison with previous results is thus impossible. In an earlier paper[1] it was shown that errors in the solubility temperature as large as 0.1° were not likely to occur if only fine crystals were present in the tube and if the rate of heating was 0.01° per minute or less; since these two precautions were taken it is thought the recorded temperatures are accurate to ±0.1°. However it is realized that various impurities might have been present in the solvent, but it would seem quite likely that the shapes of the curves relative to one another would not be greatly changed by the presence of some common impurity.

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[1] Sunier: J. Phys. Chem., 34, 2582 (1930).

Furfuryl alcohol is the poorest and n-butyl furoate the best solvent for naphthalene of any of the materials under consideration. The curve for the former solvent approximates that of n-butyl alcohol[1] as can be seen from an inspection of Fig. 2 which compares data on various aliphatic alcohols. The curve for the latter solvent is very near, if not equal to, that shown by an ideal system such as naphthalene and chlorobenzene[2] or naphthalene and ethylidene bromide.[3] The solubilities of furfuryl acetate and methyl furoate appear to be identical from 80 down to 40°; below this the latter substance dissolves a little less naphthalene.

The influence of methyl, ethyl, n-propyl and n-butyl groups is clearly seen in Fig. 1; a very regular increase in the solubility is noted for these substances. It would be of interest to study the longer chained derivatives to see if a solubility greater than the ideal would be obtained; if such were the case it is quite likely that solvation effects must be operative as Hildebrand[4] has pointed out.

It seems rather remarkable that furfuryl alcohol, containing five carbon atoms, has a solubility one might expect for normal pentanol; the former compound has a ring structure containing two double bonds and oxygen, the latter is of course a straight chain compound. It would appear that n-butyl furoate is a non-polar compound. In an earlier paper[5] the subject of polarity and solubility is discussed briefly and reference is there made to the work of Debye,[6] Smyth[7] and Stewart.[8] Further discussion does not seem necessary at this time.

Summary

The solubility of naphthalene in six derivatives of furfural has been determined at a variety of temperatures. Certain regularities have been pointed out.

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[1] Sunier: J. Phys. Chem., **34**, 2582 (1930); Ward: **30**, 1316 (1926).

[2] Ward: J. Phys. Chem., **30**, 1316 (1926).

[3] Sunier and Rosenblum: J. Phys. Chem., **32**, 1049 (1928).

[4] Hildebrand: "Solubility" (1924).

[5] Sunier: J. Phys. Chem., **34**, 2582 (1930).

[6] Debye: "Polar Molecules" (1929).

[7] Smyth: Chem. Reviews, **6**, 549 (1929).

[8] Stewart: Chem. Reviews, **6**, 483 (1929).

KINETICS OF TRANSITIONS IN POLYMORPHIC SOLIDS*

BY ARTHUR F. BENTON AND RAYMOND D. COOL

Introduction

It is well known that in chemical changes in which at least one of the reactants and one of the products is a solid phase, the reaction is commonly autocatalytic. After a longer or shorter period of "incubation," the rate increases (induction period), reaches a maximum and then decreases, finally falling off to zero when the reaction is complete. The phenomenon is interpreted on the assumption that reaction proceeds more readily at the interface between the two solid phases than elsewhere, and that the rate of reaction is proportional to the extent of this interface. The only necessary condition for the appearance of this type of autocatalysis appears to be the occurrence of a separate solid phase on each side of the reaction equation. It has been observed[1] in reactions in which one solid produces a second solid and a gas (decomposition of Ag_2O, $AgMnO_4$, $Ag_2C_2O_4$, various metallic carbonates, etc.), and in those in which a solid and a gas react to form a second solid and a gas (reduction of CuO, NiO, Ag_2O, etc., by hydrogen or carbon monoxide); it is occasionally observed in reactions in which a solid and a gas react to form a second solid (hydration of salts, oxidation of metals at low temperatures, etc.).

In addition to these three, a fourth type of reaction is available for study, namely, those in which all the participants are in the solid state. An example is the transition of a polymorphic solid, involving nothing but one solid reactant and one solid product. It appears that this case might be less complex, especially from the theoretical stand-point, than any of the other three cases cited.

Observations of allotropic transformations have indicated that in certain cases at least, reaction proceeds more readily at the boundary between the two solid phases than elsewhere.[2] It appears, however, that little attention has been given to the kinetics of allotropic changes as a function of the quantity of material transformed. Estimates of the velocity of transformation have been obtained dilatometrically in a few cases, but the assumption is usually implied that at a given temperature the rate is independent of the extent to which reaction has proceeded. Furthermore, in these experiments the solid under study was always in contact with the dilatometer liquid, which through solubility or adsorption effects might have considerable influence on the rate of reaction. In certain cases a marked effect has been observed.[3]

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* Contribution from the Cobb Chemical Laboratory, University of Virginia, No. 72.

[1] For a discussion of the results obtained in this field, see Taylor: "Treatise on Physical Chemistry," 2nd Ed., 2, pp. 1067-9.

[2] See, for example, Cohen and coworkers: Z. physik. Chem., 30, 601 (1899), 63, 625 1908); Bridgman: Proc. Am. Acad. Arts Sci., 52, 57 (1916); Early and Lowry: J. Chem. ., 115, 1387 (1919).

[3] Cohen: Z. physik. Chem., 14, 53; Cohen and Bredig: 535 (1894).

In view of these facts it was decided to study the kinetics of certain allotropic transformations by employing a dilatometer in which the volume changes are transmitted by means of an inert gas rather than by a liquid.

Experimental Method

Apparatus.—The dilatometer consisted of a glass bulb sealed at the top to a capillary tube leading to a 3-way stopcock, one arm of which was open to the atmosphere, and the other was connected to a closed vacuum manometer of 2 mm. glass capillary. The adjustment of the mercury levels in the manometer was effected by means of a mercury well and glass plunger so that the redistilled mercury was never in contact with rubber. The manometer levels were read with the help of a wood scale sliding in brass guides and counterbalanced so as to remain in any desired position. The scale carried two pointers, exactly 760.0 mm. apart, which were illuminated by small electric lights mounted on the scale. Two small mirrors, set at an angle of 45°, were also attached to the scale, one at the level of each pointer. By this device the image of the upper mercury level and pointer was brought down to the lower mirror and there reflected to the eye at the height of the lower level and pointer, thus facilitating simultaneous reading of the two levels. This somewhat complicated manometer was resorted to only after preliminary experiments with an open manometer had shown that even small fluctuations in barometric pressure were sufficient to vitiate the results.

Careful temperature control is also essential if reliable results are to be obtained. To this end, the bulb was surrounded by an electrically heated vapor bath, jacketed with asbestos paper, and tightly closed at the top with a cork stopper cemented with litharge-glycerine cement. This stopper carried a calibrated thermometer graduated to 0.1°, a narrow capillary tube by means of which air could be bubbled through the bath liquid, when necessary, to prevent bumping, and a reflux condenser. The latter was in turn connected to a 3-way stopcock so that the vapor bath could be opened to the air, or connected to a device for maintaining a constant pressure. The pressure regulator was similar to the one described by Scofield.[1]

Procedure.—A liquid whose boiling point was above the transition temperature was used in the vapor bath. For transitions from the high temperature form to the low temperature form, the bath was at first closed off from the pressure regulator, and run at atmospheric pressure to convert the sample into the high temperature form. After a suitable time the bath was connected to the regulator, in which in the meantime the pressure had been adjusted to give the temperature at which the measurement was to be made. As soon as this temperature was approximately attained, the sample, which had previously been open to the air through a calcium chloride tube, was connected to the manometer. With the mercury levels kept 760 mm. apart to insure constancy of pressure in the bulb, the rate of reaction was followed by reading the height of the mercury column in the calibrated arm of the manometer at five-minute intervals. For transitions from the low temperature form to the high, the procedure was the same, except that the preliminary heating with the bath at atmospheric pressure was not required.

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[1] Schofield: Ind. Eng. Chem., **18**, 717 (1926).

Materials.—The experiments to be reported here deal with the transitions of mercuric and of thallous iodides. These substances were chosen because their transitions occur at convenient temperatures and are accompanied, in both cases, by pronounced color changes. Samples 1-3 of mercuric iodide were used only in preliminary experiments, and their preparation need not be described. Samples 4 and 5 were made from recrystallized mercuric chloride and potassium iodide according to the procedure given in U.S. Pharmacopoeia, 8th Revision, p. 237. Sample 4 was also recrystallized from alcohol, and both samples were dried for about 100 hours in an oven at 110°.

Thallous iodide was prepared from C. P. potassium iodide and thallous nitrate. The resulting precipitate was carefully washed and dried before use.

The liquids used as vapor baths were not especially purified. Those most largely employed were water, amyl alcohol, aniline, xylene, acetic acid and benzaldehyde.

Results

Reliability of the Method.—At different times a number of trials were made to determine how closely manometer readings could be checked by displacing the mercury columns and then restoring them to a difference of 760 mm. In these trials readings could be regularly reproduced within 1 mm., and consequently in following reaction rates the manometer was read to this degree of precision only.

Table I indicates the extent to which the rate of reaction is reproducible in experiments carried out under identical conditions. In each of these runs the sample (No. 4) was first heated for one hour at 137° to convert it into the yellow form, and the rate of transition to the red form measured at 120.2°. It should be mentioned, however, that the reproducibility was by no means always so satisfactory as in Runs 31-4, owing to slight fluctuations in the temperature of the vapor bath. Fortunately, this difficulty was serious only when water or benzaldehyde was used as bath liquid.

TABLE I

Reproducibility of Rate Measurements

Run	Time to reach max. rate (min.)	Rate at max. (cm/5 min.)	Time for complete reaction (min.)	Total reaction (cm.)
31	35	1.0	75	7.4
32	35	1.1	75	7.7
33	35	1.2	65	7.9
34	35	1.1	75	7.8

In order to secure reliable information regarding the early stages of reaction, careful studies were made to determine the time required for temperature equilibrium to be established throughout the sample after the temperature of the bath had been suddenly changed. This was accomplished by observation of the manometer when the temperature was changed to the same extent as in a regular run, but without passing through the transition temperature, and also, in some cases, by comparison of the readings of the thermometer in the vapor bath with a second thermometer inserted in a well at the center of the sample. It was found that equalization of temperature required 15 min. for mercuric iodide, Sample 4 (bulb 13 cm. long and 1.8 cm. in inside diameter), 5 min. for mercuric iodide, Sample 5 (bulb 132 cm. long and 0.5 cm. in diameter, wound in a spiral), 10 min. for thallous iodide, Sample 1 (bulb 1.5 cm. in diameter), and 10 min. for thallous iodide, Sample 2 (bulb consisting of three branches, each 12 cm. long and 1.5 cm. in internal diameter).

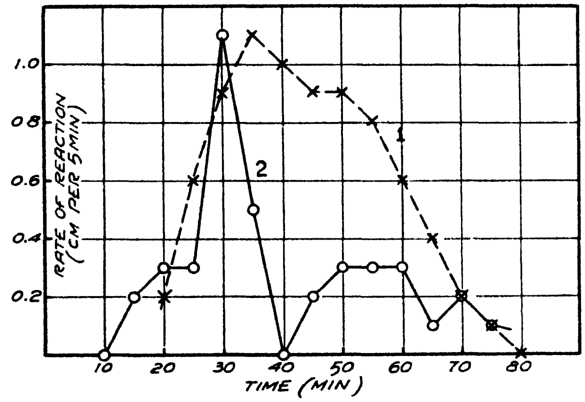

FIG. 1

Rate of transition of mercuric iodide.
Curve 1: Sample 4, yellow to red at 120.2°;
Curve 2: Sample 5, red to yellow at 130.0°.

Autocatalytic Nature of the Reactions.— Typical data from runs made under the best conditions are plotted in Figs. 1 and 2. Fig. 1 shows the rates of transition of mercuric iodide in both directions; Curve 1 represents the change, yellow to red, for Sample 4 (76.50 g.) at 120.2°, and Curve 2 represents the change, red to yellow, for Sample 5 (67.85 g.) at 130.0°. In Fig. 2 similar data are shown for thallous iodide; Curve 1 is the change, red to yellow, for Sample 1 (48.21 g.) at 142.0°, and Curve 2 is the change, yellow to red, for Sample 2 (107.61 g.) at 180.5°. On each curve the initial plotted point represents the first reading unaffected by temperature lag.

It will be seen that these transformations are autocatalytic in nature, and give curves of the same type as those for other systems involving two separate solid phases. The rate increased rather rapidly to a maximum and then fell off much less abruptly, so that only about 20-30% of the total change had occurred when the maximum rate was reached. This behavior ordinarily indicates that the reaction started and spread from a comparatively large number of centers. That this was the case was evident from visual observation of the colors of the samples as reaction proceeded. The process was never observed to start in only one or two places and spread from these, but spots of the stable form appeared throughout and then continued to grow in size, finally merging into one another. In line with these observations also is the fact that the period of "incubation" was usually very short or entirely absent, except when the subsequent rate was very slow.

Rate of Reaction and Temperature.—The rate of reaction was found to increase with increasing distance from the transition temperature, both above and below. The relative rates are indicated in three ways: (1) time required for rate to reach the maximum, (2) the rate of change at the maximum, and (3) time required for completion of the total change. Table II contains typical data for the yellow → red transition of mercuric iodide (Sample 4), where the preliminary treatment of the sample was approximately the same in each case. (The transition temperature is near 127°).

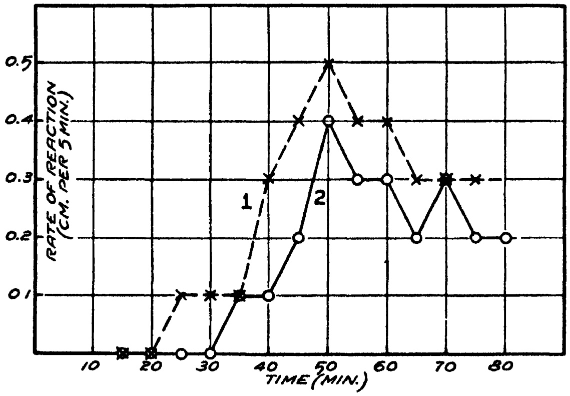

FIG. 2

Rate of transition of thallous iodide, Sample 1
Curve 1: red to yellow at 142.0°;
Curve 2: yellow to red at 176.0°

TABLE II

Yellow to Red Transition of Mercuric Iodide.

Run	Temp. °C.	Time to reach maximum (min.)	Rate at maximum (cm./5 min.)	Time for total reaction (min.)
23	98.5	<15	>8.0	25
24	116.0	45	1.0	85
30	120.2	55	0.9	105

Although changes at temperatures far removed from the transition temperature were too rapid for quantitative study, they could be followed qualitatively by observing the color change. The yellow form (Sample 1), on cooling to 50°, changed completely to red in less than 15 minutes. On cooling the yellow form (Sample 3) from 137° to 20°, it became completely red in less than 10 minutes, and a similar result was obtained on cooling it from 180° to 20°. At 122.8° this sample was less than one-third converted to the red form in 2.5 hours.

For the conversion of mercuric iodide to the high temperature form, it was found that at 129.5° Sample 3 changed to yellow only very slightly in 10 hours; at 136.7° the change required 40 minutes for completion, while at 181° reaction was complete in 10 minutes.

For thallous iodide the effect of temperature over the corresponding range is even greater. Table III shows results obtained with Sample I for the change, red to yellow. The preliminary treatment was substantially the same in each case. (The transition temperature is probably between 160° and 170°).

TABLE III

The Red to Yellow Transition of Thallous Iodide

Run	Temp. °C.	Time to reach maximum (min.)	Rate at maximum (cm./5 min).	Time for total reaction (min.)
22	131.2	Too fast to measure		20
23	142.0	45	0.5	150
26	150.0	460	0.5	>790

On cooling from 180° to 25° this sample changed completely in 2 minutes.

Data for the change of the same sample of thallous iodide in the reverse direction are given in Table IV.

TABLE IV

The Yellow to Red Transition of Thallous Iodide

Run	Temp. °C.	Time to reach maximum (min.)	Rate at maximum (cm./5 min.)	Time for total reaction (min.)
11	174.0	125	0.2	>720
20	176.0	50	0.4	>145
18	177.8	25	1.0	65
15	180.2	15	2.0	25

A number of workers[1] have found that the velocity of certain transformations from the high to the low temperature form passes through a maximum as the temperature is lowered. We have obtained qualitative evidence that the same is true of the cases under consideration. Thus when samples of mercuric iodide, sealed in tubes approximately 3 × 120 mm., were converted into the yellow form by heating and then immersed in liquid air, the yellow color immediately faded to white, but no further change occurred in 70 minutes at this temperature. On then permitting the tubes to warm up in a bath of petroleum ether, the salt gradually acquired its normal yellow color at −160° to −140°, and at the same time specks of the red form began to appear at numerous points. On reaching this stage, one sample was again cooled in liquid air, with the result that the progress of the transformation was completely stopped, the yellow portions fading to white and the red parts to orange.

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[1] Gernez: Compt. rend., **100**, 1343, 1382 (1885); Tammann: "Kristallisieren und Schmelzen," (1903); Cohen and coworkers: Z. physik. Chem., **30**, 601 (1899); **33**, 57 (1900), **35**, 588 (1900).

It is evident that the rate of conversion at −191° is very small, if not zero, and that the rate must pass through a maximum somewhere between this temperature and 20°.

Effect of Preliminary Treatment.—The rates of reaction of all samples were found to increase with the number of transformations previously undergone. This increase was very marked during the first few runs with a given sample. Thus for Sample 5 of mercuric iodide, with all other factors constant, the maximum rate was five times as great in the sixth run, and seven times as great in the ninth run, as in the first. However, the activity changed less and less in successive experiments, and finally reached a constant value.

The rate of reaction was also affected by the time and temperature of heating previous to a given transformation, as may be seen from the data in Table V, which refer to Sample 4 of mercuric iodide. Previous to these experiments the sample had attained its constant maximum activity.

Table V

Effect of Preliminary Treatment

Run	Time of heating at 137°(hr.)	Temp. of run	Time to reach maximum (min.)	Rate at maximum (cm./5 min.)	Time for total reaction (min)
28	14	120.6°	85	0.4	>205
29	1	120.6°	35	0.9	125
30	5	120.2°	55	0.9	105
31	1	120.2°	35	1.0	75

Since the conversion of the red form to the yellow at 137° required less than 30 minutes for completion, the retarding effect of heating at this temperature for times in excess of one hour may be ascribed to growth of the crystals and gradual elimination of their imperfections, a process which would be facilitated by the appreciable volatility of the material. We have obtained no evidence either for or against the applicability of Smits theory of allotropy,[1] which postulates the existence in each allotropic modification of an inner equilibrium changing with temperature.

Effect of Different Gases on Rate of Transition.—Although the large majority of the runs were carried out in the presence of air, a few experiments were made with thallous iodide in atmospheres of carbon dioxide or nitrogen. Since the results were the same within experimental error for all three gases, it is concluded that the adsorption of gas by the iodide, if it occurs at all, is a negligible factor in the rate of transition.

Transition Temperatures and Changes of Volume.—While no special effort has been made in this work to determine the exact location of the transition temperatures, the results definitely place them within certain limits. Thus the transformation of mercuric iodide at atmosphere pressure must occur between 123° and 129.5°. Most of the values in the literature are 126° to 127°, but figures as high as 130° have been reported. We have found that the transition point of thallous iodide lies definitely between 150° and 174° and probably between 160° and 170°. The values recorded in the literature vary from 150° to 190°.

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[1] Smits: "The Theory of Allotropy," (1922).

From observation of the total displacement of the mercury level in the manometer when reaction was complete, and from its volumetric calibration (0.028 cc. per cm.), the change of volume accompanying these transitions was obtained, as follows: mercuric iodide, 0.0028 cc. per gram; thallous iodide, 0.003 cc. per gram. These differences in specific volume are exceptionally small. The red form has the greater density in each case.

Summary

A dilatometric method has been developed for measuring the rates of polymorphic transitions of solids in presence of an inert gas. The method eliminates the spurious effects that occur when liquids are used in the dilatometer to transmit the volume changes.

The transitions of mercuric iodide and thallous iodide have been found to be autocatalytic in both directions. The kinetics are similar to those observed in numerous other systems in which one of the reactants and one of the products is a solid phase.

Above the transition point the rates increase very rapidly with increasing temperature. For the change in the reverse direction, the rate at first increases as the temperature is lowered, but then passes through a maximum, and decreases to very small values at liquid air temperature.

The rate is markedly affected by the duration and temperature of heating of the sample previous to conversion.

Approximately equal rates are found in the presence of air, carbon dioxide or nitrogen.

University, Virginia.

REDUCTION OF SILVER HALIDES BY SODIUM SULPHITE AND NITRITE IN PRESENCE OF INDUCTORS AND A CHEAP DEVELOPER IN PHOTOGRAPHY

BY RAM BEHARI LAL VERMA AND N. R. DHAR

In previous publications[1] from these laboratories it has been shown that sodium sulphite, which readily undergoes oxidation in air or oxygen initiates or accelerates the oxidation of sodium nitrite, potassium oxalate, ferrous sulphate, cuprous, nickelous, ferrous and other hydroxides.

In photography, sodium sulphite has been largely used since its introduction by Berkeley, to prevent stains produced by the oxidation of developers in alkaline solutions. The exact function of the sulphite in development has not yet been cleared up.[2]

In this paper, the reactions between sodium sulphite and different sparingly soluble silver salts have been studied in presence of various organic and inorganic developers and an attempt has been made to find out the real mechanism of the sodium sulphite added in photographic development. The reactions, however, differ from the usual induced reactions of sodium sulphite in the fact that the oxidation of sodium sulphite is not the primary change here but a secondary one. In fact, the developers used in photography, appear to induce the reduction of the sparingly soluble silver salts by sodium sulphite.

The following reactions have been investigated:

Reduction of (1) silver chloride, (2) silver bromide, (3) silver iodide, (4) silver thiocyanate by sodium sulphite in presence of

(a) Hydroquinone.
(b) Pyrogallol.
(c) Metol.
(d) Hydroxylamine hydrochloride.
(e) Hydrazine sulphate.
(f) Ferrous sulphate.

Experimental Procedure

20 cc. of a standard solution of silver nitrate (N/99.5) were added to 20 cc. of a standard solution of sodium chloride (N/99.5) taken in a bottle and silver chloride was precipitated. 20 cc. of a standard solution of the developer was then added and the volume was made up to 100 cc. The mixture

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[1] Dhar: J. Chem. Soc., **111**, 694 (1927); Proc. Akad. Wet. Amsterdam, **29**, 1023 (1921); Z. anorg. Chem., **128**, 207 (1923); J. Phys. Chem., **28**, 943 (1924); Mittra and Dhar: Trans. Faraday Soc., **17**, 676 (1922); Z. anorg. Chem., **122**, 146 (1922); J. Phys. Chem., **29**, 376; Palit and Dhar: 799 (1925); **30**, 939 (1926); **32**, 1663 (1928); **34**, 711 (1930).

[2] Compare, "Photography as a Scientific Implement," 150 (1923).

was shaken for 20 minutes and filtered. The experiments were carried on at 30°. The precipitate remaining on the filter paper was washed several times with distilled water and nitric acid was added to it to dissolve out the silver formed by reduction. The filter paper was washed and the filtrate titrated against a standard potassium thiocyanate solution using ferric sulphate as an indicator. From this the amount of silver reduced was calculated.

In the case of silver bromide, sodium bromide was used and in the case of silver iodide, potassium iodide was used for the precipitation of the silver halides. Silver thiocyanate was precipitated with potassium thiocyanate.

In all the cases the strength of sodium sulphite was N/24.3. Tables I-III show the experimental results:

TABLE I

Hydroquinone M/200

Na_2SO_3 present cc.	AgCl present gm.	Ag. obtained gm.
0	0.02881	0.00144
5	”	0.00621
10	”	0.00909
15	”	0.01170
20	”	0.01674

TABLE II

Hydroquinone M/400

Na_2SO_3 present cc.	AgCl present gm.	Ag. obtained gm.
0	0.02881	0.00126
5	”	0.00450
10	”	0.00810
15	”	0.01008
20	”	0.01125

TABLE III

Hydroquinone M/800

Na_2SO_3 present cc.	AgCl present gm.	Ag. obtained gm.
0	0.02281	0.00099
5	”	0.00342
10	”	0.00657
15	”	0.00729
20	”	0.00872

From the foregoing results we see that the amount of AgCl reduced decreases as the concentration of the solution of the developer decreases but increases in all the cases as the amount of Na_2SO_3 increases.

Exactly similar results have been obtained with other developers and various silver salts.

The above results show that silver chloride is reduced by the developer solution even in the absence of sodium sulphite. Similar results are obtained with other silver salts also. The greatest reduction is observed with metol and the least with ferrous sulphate.

The results in Table IV will show that in the absence of sodium sulphite, the reducing power of the developer is in the following decreasing order:

Metol >Pyrogallol >Hydroquinone >Hydrazine sulphate >Hydroxylamine hydrochloride >Ferrous sulphate.

TABLE IV

	Amount of Ag. reduced from			
M/200	AgCl	AgBr	AgI	AgCNS
Metol	0.00216	0.00359	0.00054	0.00045
Pyrogallol	0.00207	—	0.00045	0.00027
Hydroquinone	0.00144	0.00351	0.00045	0.00022
Hydrazine sulphate	0.00063	0.00063	0.00013	—
Hydroxylamine hydrochloride	0.00027	0.00054	—	0.00018
Ferrous sulphate	—	0.00052	0.00009	—

As has been mentioned before, if no developer is used, sodium sulphite does not reduce the silver salts and hence the silver salts are the actors. From the results it will be seen that even without the sodium sulphite the developers reduce the silver salts (though to a slight extent), and hence are called the inductors. Sodium sulphite in its turn is the acceptor.

It is remarkable that in the presence or in the absence of sodium sulphite, the reduction of silver salts with the organic developers is greater than with the inorganic developers of the same concentration.

If the reduction by sodium sulphite be considered in presence of the inductors the inducing powers of these inductors come out in the same order in which they reduce the silver salts in the absence of sodium sulphite:—

Metol >Pyrogallol >Hydroquinone >Hydrazine sulphate >Hydroxylamine hydrochloride >Ferrous sulphate.

The results in Table V will illustrate this point.

The results quoted in Table V are those in which 20 cc. of sodium sulphite were used.

Another thing to be noted from the results is that the greatest reduction is in the case of chlorides and the least in the case of iodides i.e. the order is AgCl > AgBr > AgCNS > AgI. The reason for this may be that silver iodide is the least soluble and silver chloride is the most soluble of the silver salts investigated.

These results show that the reduction of the silver salts by sodium sulphite can take place only in the presence of substances which themselves can reduce the silver salts. It appears that these inductors in being oxidised

TABLE V

Salt	Inductor	M/200	M/400	M/800
AgCl.	Metol	0.02133	0.01935	0.01782
	Pyrogallol	0.02052	0.01611	0.00792
	Hydroquinone	0.01674	0.01125	0.00872
	Hydrazine sulphate	0.01377	0.00918	0.00729
	Hydroxylamine hydrochloride	0.00981	0.00549	0.00270
	Ferrous sulphate	0.00675	0.00486	0.00270
	II			
AgBr.	Metol	0.01872	0.01782	0.01269
	Pyrogallol	0.0144	0.00846	0.00450
	Hydroquinone	0.00999	0.00702	0.00477
	Hydrazine sulphate	0.00369	0.00342	0.00306
	Hydroxylamine hydrochloride	0.00369	0.00306	0.00288
	Ferrous sulphate	——	0.00261	0.00153
	III			
AgI.	Metol	0.0009	0.00085	0.00072
	Pyrogallol	0.0009	0.00063	0.00054
	Hydrazine sulphate	0.000315	0.000270	0.000225
	Hydroxylamine hydrochloride	0.00045	0.000270	0.000225
	IV			
AgCNS.	Metol	0.01449	0.01251	0.00909
	Pyrogallol	0.00576	0.00261	0.00198
	Hydroquinone	0.00198	0.00117	——
	Hydrazine sulphate	0.00036	0.00027	——
	Hydroxylamine hydrochloride	0.00036	0.00027	——

start the oxidation of sodium sulphite by the silver salts and when once the oxidation of sodium sulphite is started, it goes on reducing the silver salts when its concentration is increased.

For instance metol reduces the silver salts thus:

Metol + silver chloride = silver + oxidation product of metol.

This primary reaction starts the oxidation of sodium sulphite according to the following equation:

$$Na_2SO_3 + 2AgCl + H_2O = Na_2SO_4 + 2Ag + 2\ HCl,$$

the reduction by sodium sulphite being a secondary change. Similarly for the other reactions primary and secondary reactions occur.

In all these cases, the primary change, i.e. the oxidation of the easily oxidisible substances, pyrogallol, metol etc. takes place and this primary change induces the secondary or the induced reaction i.e. the oxidation of sodium sulphite by the silver salts. The view that hydroquinone can act as an inductor and sodium sulphite as the acceptor has also been advanced by Bancroft.[1]

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[1] J. Phys. Chem., 33, 1188 (1929).

We have observed that sodium nitrite can also behave as an acceptor in a similar way in the reduction of the silver salts in the presence of inductors such as metol, hydroquinone and pyrogallol. Sodium nitrite alone does not reduce the silver salts. The experimental results are given in Table VI.

TABLE VI

N/200 $NaNO_2$ added cc.	AgCl present gm.	Ag. reduced gm.
	I. M/100 Hydroquinone	
0	0.02881	0.00189
5	"	0.00324
10	"	0.00387
15	"	0.00432
20	"	0.00486
	II. M/200 Hydroquinone.	
0	.02881	0.00144
20	"	0.00369
	III. M/400 Hydroquinone.	
0	0.02881	0.00108
20	0.02881	0.00270

The results with Metol are given in Table VII.

TABLE VII

$NaNO_2$ added cc.	AgCl present gm.	Ag. reduced gm.
	M/100 Metol	
0	0.02881	0.00252
5	"	0.00360
10	"	0.00423
15	"	0.00468
20	"	0.00540
	M/200 Metol	
0	0.02881	0.00216
20	"	0.00423
	M/400 Metol	
0	0.02881	0.00171
20	"	0.00324

This result very well bears out the observation of Dhar[1] that one chemical change will either promote or induce another chemical change of the same nature. The reduction of the silver salts by metol, etc. brings about their reduction by sodium nitrite.

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[1] Proc. Akad. Wet. Amsterdam, 29, 1023 (1921).

The reduction may be represented in the following way:

$\mathrm{AgCl} + \text{metol} = \mathrm{Ag} +$ oxidation product of metol (primary change)

$2\ \mathrm{AgCl} + \mathrm{NaNO_2} + \mathrm{H_2O} = 2\mathrm{Ag} + \mathrm{NaNO_3} + 2\ \mathrm{HCl}$ (secondary change)

It is interesting to note from the results that of all the organic developers the best inductor is metol and this is followed by pyrogallol and hydroquinone. This is probably due to the side chain present in metol.

Of the inorganic developers hydrazine sulphate is more reducing than hydroxylamine hydrochloride or ferrous sulphate.

We have carried on some experiments to prove the practical use of the reduction of silver salts by sodium sulphite. We have tried to show experimentally that sodium sulphite plays an important part in the development in photography. It has been observed that the efficiency of the developer is well maintained even when the amount of metol is considerably decreased and the amount of sodium sulphite is largely increased. Photographic plates were used and the developing solutions containing different amounts of sodium sulphite were utilised.

The developing solution used in practice has the following composition:

$$\text{I.}\quad \left.\begin{array}{r}\text{1 gm. metol}\\ \text{4 gms. hydroquinone}\\ \text{25 gms. }\mathrm{Na_2SO_3}\end{array}\right\}\text{ in 500 cc. water}$$

II. 25 gms. $\mathrm{Na_2CO_3}$ " " "

Equal volumes of the solutions from the two are taken and the plate is developed in the mixture.

In our experiments two photographic plates were exposed for the same time and the one developed in the above solution and the other developed in the solution consisting of

$$\text{I.}\quad \left.\begin{array}{r}\text{0.5 gm. metol}\\ \text{50 gms. }\mathrm{Na_2SO_3}\end{array}\right\}\text{ in 500 cc. water}$$

II. 25 gms. $\mathrm{Na_2CO_3}$ do.

It is found that in the case when the amount of the metol is reduced to one half, hydroquinone eliminated altogether, and sodium sulphite being doubled, the development is as satisfactory as in the previous case but it is a bit slow.

Another proportion was tried with the following combination:

$$\text{I.}\quad \left.\begin{array}{l}\text{0.5 gm. metol}\\ \text{2 gm. hydroquinone}\\ \text{37.5 gms. }\mathrm{Na_2SO_3}\end{array}\right\}\text{ in 500 cc. water}$$

II. 25 gms. $\mathrm{Na_2CO_3}$ do.

This formula worked quite well, though the development was again a bit slow.

The cause of the slow development, in cases where more sodium sulphite is due to its retarding influence on the reduction of silver salts by hydroquinone or metol.

It has been established by Dhar,[1] Moureu and Dufraisse[2] and others that many negative catalysts in oxidation reactions actually take place in the chemical changes with the oxidizing agents. It appears, therefore, that sodium sulphite can very well partially replace the expensive developer metol or hydroquinone.

Summary

1. The reduction of AgCl, AgBr, AgI and AgCNS by Na_2SO_3 in presence of organic substances like metol, hydroquinone, pyrogallol and inorganic substances like hydroxylamine hydrochloride, hydrazine sulphate and ferrous sulphate has been studied.

2. It has been observed that in the absence of metol, pyrogallol etc., there is no reduction of the silver salts by sodium sulphite alone but metol, pyrogallol, etc., are capable of reducing silver salts in the absence of sodium sulphite. The reducing power is in the following decreasing order:

Metol > Pyrogallol > Hydroquinone > Hydrazine sulphate > Hydroxylamine hydrochloride > Ferrous sulphate.

3. The reduction of the silver salts is increased both by increasing the concentration of the developers as well as that of sodium sulphite. The inducing action of the developers on the reduction of silver salts by sodium sulphite has been shown to follow the same order as was obtained for the reduction of silver salts by the developers alone.

4. Of all the silver salts the greatest reduction has been observed in the case of chlorides and the least in the case of iodide, the order being AgCl > AgBr > AgCNS > AgI.

5. The mechanism of these reactions has been explained.

6. Reactions of a similar type have also been carried out by using sodium nitrite instead of sodium sulphite.

7. It has been shown by exposure and development of plates that in the existing formula for developers, the amount of such expensive substances as metol, hydroquinone etc. can be profitably diminished if the quantity of Na_2SO_3 is increased.

8. It has been observed that as the quantity of the Na_2SO_3 is increased the rate of the reduction of the photographic plates is diminished owing to the fact that acceptors like Na_2SO_3 begin to act as marked negative catalysts when used in higher concentrations.

Chemical Laboratory,
Allahabad University,
Allahabad, India,
January 29, 1931.

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[1] Proc. Akad. Wet. Amsterdam, **29**, 1023 (1921).

[2] Compt. rend., **179**, 237 (1924).

REDUCTION REACTIONS IN SILICA GELS

BY DALLAS S. DEDRICK

Gels of the silicic acid type have been characterized[1,2] as rigid, transparent systems having a continuous but very porous solid phase; a continuous liquid phase fills the interstices of the solid. The liquid phase may exist as free liquid or as liquid adsorbed on the surface of the solid phase, or as part of the crystal lattice itself. Diffusion of solute takes place readily through this liquid phase. The chemical composition of the solid phase does not affect diffusion or reaction phenomena within the system.[3]

Clark[4] points out that, in general, freshly prepared silica gels are in a mesomorphic state. They show a paracrystalline structure which on standing undergoes slow changes by means of a regular orientation which must be due to the progressive arrangement of the silicon dioxide molecules into a crystal lattice. Hence, in time, the very small capillary structure must slowly disappear in favor of the regular crystalline structure. This statement is borne out by Röntgen analysis of old silica gels.

Reactions in gels are interesting because the gel structure affords a medium in which no convection currents are produced by the diffusion of the reagents into the system. The purpose of the present investigation was to study oxidation and reduction reactions in an alkaline gel system and to note the influence of the concentrations of the reactants as well as the influence of the gel structure itself on the nature and behavior of the products formed.

Materials and Methods

Because of its slight change in solubility with temperature a silicic acid gel cannot be prepared by cooling a hot solution, but it must be made by the interaction of an acid with a soluble silicate either directly or by dialysis. The gels used in this study were basic in their reaction. Owing to the fact that gelation takes place rapidly from an alkaline solution, it is necessary to mix the reagents directly in the reaction tubes. Calculated quantities are admitted by means of burettes and care is taken to insure thorough mixing and removal of air bubbles before the system sets. The quantities of the reagents used must be very carefully regulated since it was noted that very slight variations from the calculated amounts produce unsatisfactory gels. The gels were prepared and observed in eight inch tubes.

Two concentrations of sodium silicate were used in the preparation of the gels, one having a specific gravity of 1.10 and the other 1.06. They were

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[1] Jordan Lloyd: Biochem. J., **16**, 530 (1922).

[2] van Bemmelen: Z. anorg. Chem., **20**, 265 (1902).

[3] Dreaper: J. Soc. Chem. Ind., **32**, 6781 (1913).

[4] Clark: Applied X-rays," 174 (1927).

prepared by diluting ordinary commercial "water glass." All other reagents were either of C.P. quality, or they were specially purified before use. The sulfur dioxide solutions were prepared by passing the gas into distilled water at 0°C. immediately before use.

Throughout this work gelation was produced by sulfuric acid in which calculated amounts of copper sulfate had been dissolved. Gels of three types were prepared using 3N, 1.5N, and 0.75N sulfuric acid, respectively. The copper sulfate concentrations were 1 g., 0.5 g. and 0.25 g. in 30 cc. gel.

After the gels had stood for a day a 10 cc. portion of the reducing agent was added to each tube. The speed of diffusion of the reagent was obtained by noting from time to time the distance through which the reaction band had moved. The readings were made by means of a gauge and are accurate to within less than 1 mm.

The possibility of untrustworthy comparisons caused by non-uniform handling was carefully avoided. In the analysis of the products standard qualitative analytical methods were used.

Results

A distinct qualitative difference is noted in the reducing properties of two percent and one percent aqueous solutions of hydroxylamine hydrochloride. The reaction product in either case is composed of a mixture of red cuprous oxide and minute copper crystals which give a decided metallic luster to the precipitate. The more pronounced effects are noted when the one percent solution is allowed to diffuse through the system. Here, the reduction products are invariably precipitated in the form of Liesegang's rings. No evidence of the banding of the reaction products is observed in the case of the systems reduced by the two percent hydroxylamine solution.

Gels made from the more dilute solution of sodium silicate were invariably more satisfactory. Variation in the concentration of the cupric ion or the concentration of the acid used in making the gel appear to have little influence.

Gels through which a 1 M aqueous solution of sulfur dioxide is diffusing show quite interesting phenomena. Within a few minutes after the addition of the reducing agent there appears a distinct brownish-yellow band containing cuprous oxide. This band moves progressively downward through the gel. Tables I and II show the movement of this band measured in representative gels prepared from sodium silicate with a specific gravity of 1.06. Among the gels listed in these Tables are those prepared by means of three different concentrations of acid and also containing three different concentrations of cupric sulfate. The curves in Fig. 1 are obtained by plotting the mean values of the movement of the band against the time in hours. The results for the dilute gel are shown graphically by Curve 2 Fig. 1. The rate of movement through the concentrated gels is shown in Table III and in Curve 1 of Fig. 1. The two curves lie quite close together. It is to be noted that during the first twenty hours, the diffusion is faster in those gels prepared from the more concentrated silicate solution. After this the curves lie parallel to one another, indicating equal rates of diffusion.

TABLE I

Distance moved by Ring in Cms.

	Hours		14	39	63	87	111
No.	Conc. Acid	Conc. $CuSO_4$					
18	3 N	1.00	2.1	3.6	4.5	5.1	5.7
23	3 N	0.50	2.2	3.8	4.7	5.3	5.9
28	3 N	0.25	2.2	3.8	4.6	5.3	5.9
48	1.5 N	1.00	2.1	3.5	4.5	5.2	5.8
53	1.5 N	0.50	2.3	3.6	4.7	5.3	5.9
58	1.5 N	0.25	2.2	3.7	4.8	5.2	5.7
78	0.75N	1.00	2.2	3.5	4.5	5.2	5.8
83	0.75N	0.50	2.2	3.6	4.6	5.2	5.7

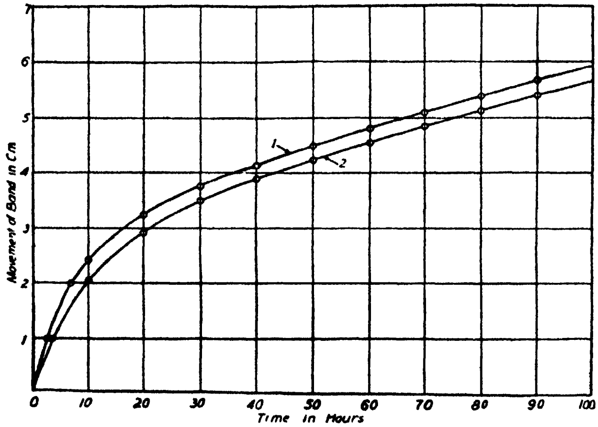

FIG. 1

TABLE II

	Hours		.75	18.5	30.5	45.5	76
No.	Conc. Acid	Conc. $CuSO_4$					
106	1.5N	0.4	0.7	2.9	3.5	4.0	4.7
107	1.5N	0.4	0.7	2.9	3.5	4.1	5.0
108	1.5N	0.4	0.7	2.9	3.5	4.1	5.1
109	1.5N	0.4	0.7	3.0	3.7	4.2	

TABLE III

	Hours		7.5	25.5	37.5	52.5	83
No.	Conc. Acid	Conc. $CuSO_4$					
101	1.5N	0.7	2.4	3.8	4.0	4.9	5.9
102	1.5N	0.7	2.2	3.3	3.9	4.5	5.3
104	1.5N	0.7	2.2	3.6	4.0	4.6	5.7
105	1.5N	0.7	2.2	3.7	4.0	4.8	5.8

After about four days the formation of small crystals of cuprous oxide was observed in the area through which the sulfurous acid had already passed. These crystals differ from those first formed in that they are red instead of yellowish brown and that they are promiscuously scattered throughout the gel. The crystals grow quite rapidly and they are well defined; they are always more numerous and larger near the bottom of the tube. Initially the crystals have the form of a cross, but as they grow larger other appendages appear until the full-grown crystal is composed of eight well defined projections. Fig. 2 gives a view of the unordered arrangement of the crystals in the gel. Fig. 3 is a view of a typical crystal magnified twenty times.

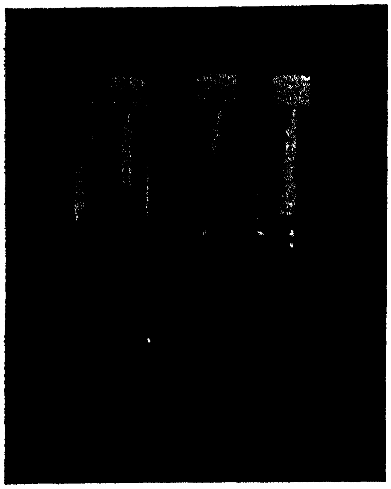

FIG. 2

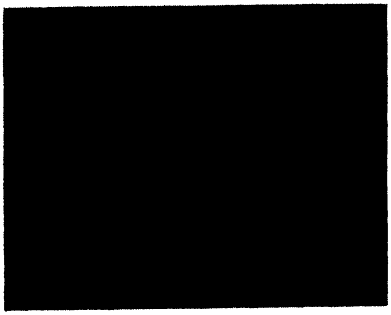

FIG. 3

The crystals belong to the orthorhombic system. Under the microscope they appear to be distinctly fibrous. Analysis shows them to be cuprous oxide. They differ structurally, however, from cuprite which is the most common natural form of cuprous oxide. After a period of two years these crystals under an atmosphere of sulfur dioxide have disintegrated into crystal groups of metallic copper. These small crystals are so arranged that the group has the same geometrical shape as the crystal of cuprous oxide from which it was formed.

A distinct Fehling's test is observed as a result of the diffusion of a 5 percent glucose solution into those gels made from the more dilute solution of sodium silicate. The product consists of yellow cuprous oxide. No reaction is noted upon the addition of the glucose solution to those gels made from the more concentrated sodium silicate.

Discussion

The fact that the more dilute solution of hydroxylamine gives a banded structure while the more concentrated solution does not is in agreement with the results obtained by Holmes[5] and by Bradford.[6] According to

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[5] Holmes: J. Am. Chem. Soc., **40**, 1187 (1918).

[6] Bradford: Biochem. J., **10**, 169 (1915).

Bradford, striations in gels are formed only by interaction of dilute reagents. Since the reaction product is precipitated from a supersaturated solution it is necessary that the reagents be dilute in order to allow any distance between areas of supersaturation.

Better results are observed throughout when the more dilute solutions of sodium silicate are used in the preparation of the gels. This is due to the fact that the gels so prepared become homogeneous more quickly. A gel so prepared is less brittle than a gel made from a more concentrated silicate solution and is less affected by the stresses incident to gelation. It is quite possible that the paracrystalline state postulated by Clark[4] is more prolonged in the case of the gels made from the more concentrated silicate solution. This would account for the more rapid initial rate of diffusion through a gel so prepared. As is shown by the curves, after the first twenty hours the rates of movement of the reaction bands are equal for both types of gels. This indicates that the molecular or crystal arrangements are quite comparable in the two gels after that time.

An indication as to the structure of the gel is given by the fact that a 5 percent glucose solution will diffuse into a gel made from a sodium silicate solution with a specific gravity of 1.06, but will not diffuse into a gel prepared from the more concentrated silicate solution, this is shown by the absence of the Fehling's test in the tube. This phenomenon indicates that there must be interstices in the one gel which are of a diameter sufficiently large to allow passage of the glucose molecules while in the other there are not. The failure of glucose to diffuse into the more concentrated gel cannot logically be attributed to differences in concentrations which would affect the osmotic relations. According to Pringsheim,[7] osmotic forces are exerted through the medium of a very thin film of precipitate. The reaction stops at the surface if the solutions are isotonic. There is no indication of a reaction in either the supernatant glucose solution or in the gel itself. No reaction occurs when salts are added to the glucose solution to insure its being hypertonic with respect to the cupric surface in the gel. Hence, it is evident that the failure to react within the gel is not due to an isotonic condition.

From a study of the vapor pressures of different liquids absorbed in silica gels, Anderson[8] calculates the diameters of the largest capillaries to be of the order of 5×10^{-6}cm. According to Patrick,[9] we must assume that the pores must approach molecular magnitudes in order to account for the pronounced lowering of vapor pressures above silica gels. However, there is no data at hand showing the effect of different concentrations of gel on the vapor pressure lowering. It does not appear illogical, however, to postulate a pore diameter in the gels made with the more concentrated sodium silicate solution which is smaller than the diameter of the glucose molecule.

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[7] Pringsheim in Alexander: "Colloid Chemistry," 790 (1926).

[8] Anderson: Z. physik Chem., 88, 191 (1914).

[9] McGavick and Patrick: J. Am. Chem. Soc., 42, 946 (1920).

The apparent movement of the reaction bands downward through the gels in those cases where sulfur dioxide solution is the diffusing agent is due to alternate precipitation and solution. The reduction products in alkaline solution are soluble in the acid that diffuses through the gel after the base has been neutralized. The diffusion curves for sulfurous acid are parabolic in shape which is in agreement with the findings of Moravec.[10]

The product of the alkaline reduction of cupric sulfate with sulfurous acid is the yellow hydrated cuprous oxide. This precipitate is quite stable in air, even at elevated temperatures. At higher temperatures the gel-free precipitated cuprous oxide samples fused into copper globules in the reducing flame and changed to a mixture of black cupric oxide and red cuprous oxide in the oxidizing flame. This yellow form of the oxide is quite soluble in sulfurous acid. For this reason the reaction band is never very wide because solution takes place almost as rapidly as precipitation.

The cuprous oxide crystals form with no apparent relation to each other and in no sense could they be considered to form banded structures in the gel body. Obviously, the conditions which bring about the crystallization are not the same as those which caused the original banded precipitates. There is undoubtedly a diffusion of cuprous ion in the wake of the moving sulfurous acid which tends to concentrate the cuprous ion in the lower half of the tube. The crystal formation is, therefore, due to precipitation from a supersaturated solution of cuprous oxide.

Summary

A study has been made of the reduction of cupric ions in silica gels.

Hydroxylamine reduces the cupric ion to the cuprous ion and metallic copper. A one percent solution causes the formation of well defined crystals in banded rings. The two percent solution does not form banded precipitates.

Evidence is presented that in a five percent glucose solution the molecules are of such magnitude as to be larger than the interstices of a gel prepared from sodium silicate having a specific gravity of 1.10. The molecules are smaller, however, than the interstices of a gel prepared from the more dilute silicate, (1.06).

A solution of sulfur dioxide in water diffuses rapidly into the alkaline gels causing the precipitation of a band of yellow, metastable cuprous oxide. This oxide is soluble in the sulfurous acid which diffuses through the gel after the precipitation of the product. In acid solution, the oxide is reprecipitated as well-defined crystals of red cuprous oxide.

During the first twenty hours the rate of diffusion of sulfur dioxide solution into the more concentrated gel is greater than the rate of diffusion of an identical solution through a gel prepared from the more dilute silicate solution. After approximately twenty hours the rates of diffusion are equal.

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[10] Moravec: Kolloid-Z., **49**, 39-46 (1929).

This indicates that at the beginning the more concentrated gel is structurally different from the more dilute gel, but that after that time, the two gels become structurally comparable. The general shape of the curve is in agreement with that found by Moravec.

Variations of factors other than the concentration of the sodium silicate produce no effect on the rate of diffusion of sulfur dioxide solution through the gels. A variation due to concentration changes would undoubtedly be noted if the reagents were more dilute.

Acknowledgment is made to Dr. J. L. Whitman, now of Texas Christian University for suggestion and supervision of the problem.

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THE ADSORPTION OF HYDROGEN BY NICKEL POISONED WITH CARBON MONOXIDE*

BY T. A. WHITE AND ARTHUR F. BENTON

Introduction

It has been recognized for some years that the reactions which occur at the surface of a solid catalyst are intimately connected with the nature and extent of the adsorptions of the reacting substances and products by the catalyst. While all gaseous reactions involve two or more gases, adsorption studies have largely been concerned with one gas at a time. In order to have a complete picture of the process occurring at the solid surface, all the gases involved should be considered simultaneously. This has been done to some extent with catalytically inactive materials, and to a lesser extent with active catalysts.

One of the most interesting facts concerning the catalytic activity of a substance is the inhibiting action which a small amount of a foreign gas can have on the activity of the catalyst. The inhibitory action of carbon monoxide on various metallic catalysts[1] has been known for a long time. Pease and Stewart[2] have studied the poisoning effect of carbon monoxide on the hydrogen-ethylene reaction with a copper catalyst. In studying the effect of small amounts of carbon monoxide on the adsorption of hydrogen and ethylene by copper, Griffin[3] found that adsorptions were increased at lower pressures and decreased at higher pressures.

Since nickel is a very active hydrogenation catalyst, it appeared to us that it would throw considerable light on the adsorption problem if the effect of carbon monoxide on the hydrogen adsorption of nickel was studied. It is known that carbon monoxide is a marked poison to a nickel catalyst.[4] By making such a study we hoped, also, to see if the effect Griffin observed was peculiar to copper or if it was a property of all catalysts.

Experimental Method and Apparatus

The initial results were obtained with the usual type of apparatus, which has been described by Pease;[5] a new apparatus, in which stop-cocks are largely eliminated, was employed in obtaining the later results. The details of apparatus, procedure, materials, constant temperature baths and free space determinations have previously been described.[6]

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* Contribution from the Cobb Chemical Laboratory, University of Virginia, No. 70

[1] Henry: Phil. Mag., 65, 269 (1825).

[2] Pease and Stewart: J. Am. Chem. Soc., 47, 1235 (1925).

[3] Griffin: J. Am. Chem. Soc., 49, 2136 (1927).

[4] Green: "Industrial Catalysis," p. 305.

[5] Pease: J. Am. Chem. Soc., 45, 1197 (1923).

[6] Benton and White: J. Am. Chem. Soc., 52, 2325 (1930).

The small amounts of carbon monoxide that were used were always placed in the adsorption bulb, which was at the required temperature, half an hour before the regular run was started. Between runs the adsorbent was evacuated for about two hours, at 200° in the case of the first adsorbent, and at 250° for the second of the two used. The first adsorbent, which was the same as the first adsorbent already used by us,[6] weighed 23.68 g., and the second weighed 23.03 g. Both were prepared from the nitrate as previously described. Helium, assumed to be unadsorbed, was used as a reference gas. Carbon monoxide was prepared by the reaction of formic acid with sulphuric acid and purified by passage over soda-lime and phosphorus pentoxide.

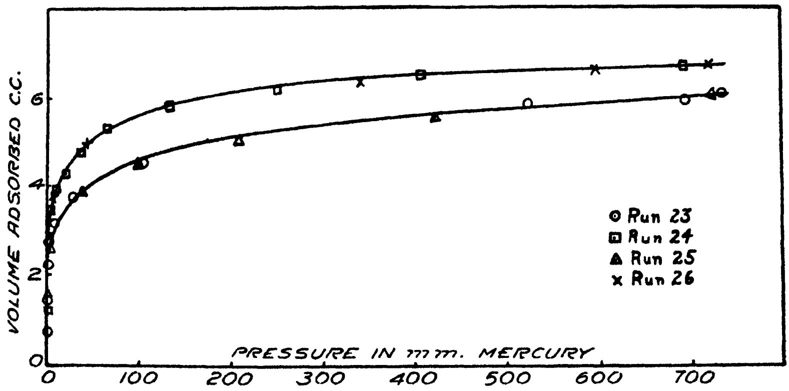

FIG. 1

Adsorption of hydrogen by nickel poisoned with carbon monoxide at 0°. Run 23, hydrogen with no CO; Run 24, hydrogen with 0.038 cc. CO; Run 25, hydrogen with no CO; Run 26, hydrogen with 0.038 cc. CO.

The small amounts of carbon monoxide were measured in two ways, both of which were essentially the same. In the earlier apparatus, it was possible to measure volumes as small as 0.038 c.c. by knowing the volume of the bore of a given stop-cock and filling it with carbon monoxide at a known pressure and temperature. In the later form of apparatus, the volumes of carbon monoxide were measured in the calibrated capillary tube,[6] F, at a known pressure and temperature.

Expermental Results

Fig. 1 shows a series of isotherms for Sample 1. While the same effect was obtained with other samples of nickel, none of them gave such a marked increase in adsorption, all along the isotherm, when carbon monoxide was used. This increase could only be obtained with a fresh sample of nickel which had not previously been exposed to carbon monoxide. It was impossible to be sure that the carbon monoxide was pumped off after a given run. For example, Run 25 checked Run 23, both of which were made with pure hydrogen; and Run 26 checked Run 24, in each of which 0.038 c.c. of carbon monoxide had been taken up by the adsorbent. But Run 27, which was supposed to be a pure hydrogen run, checked Runs 24 and 26, indicating that the carbon monoxide might have remained adsorbed in spite of the evacuation following Run 26. This same type of thing was encountered with Sample 2; an increase was obtained at first, but could not be checked in subsequent runs.

Larger amounts of carbon monoxide, close to a tenth of a cubic centimeter, produce no marked effect on the hydrogen adsorption. The isotherms of pure hydrogen and those with approximately 0.1 c.c. of carbon monoxide present lie so close to each other that it is doubtful if the differences exceed the experimental error. However, it may be that there is a slight increase in the hydrogen adsorption all along the isotherm when this quantity of carbon monoxide is used.

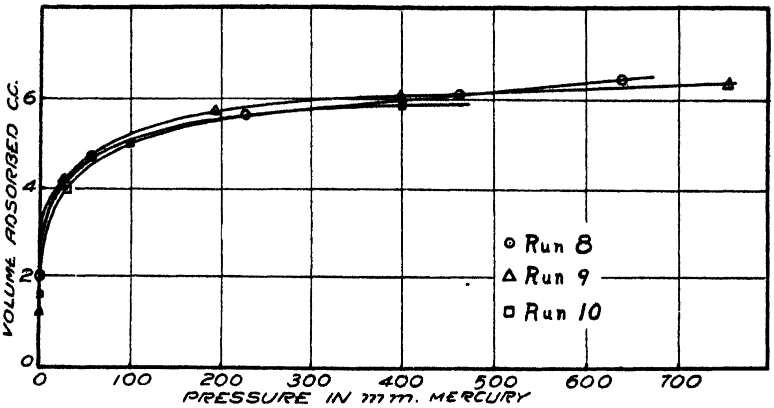

FIG. 2

Adsorption of hydrogen by nickel poisoned with carbon monoxide at 0°. Run 8, hydrogen with 0.3 cc. CO; Run 9, hydrogen with 0.8 cc. CO; Run 10, hydrogen with 1.6 cc. CO.

The isotherms given in Fig. 2 show the effect of larger amounts of carbon monoxide on the hydrogen adsorptions of Sample 2. Run 9 agrees very closely with the pure hydrogen isotherm. Runs 1-7 were made with small amounts of carbon monoxide, and checked satisfactorily the results obtained with Sample 1. It will be noticed that larger amounts of carbon monoxide produce no striking changes in the type of isotherm or in the amounts adsorbed. However, the rate at which equilibrium is reached in these last three cases is slower the greater the amount of carbon monoxide employed.

These experiments were extended to lower temperatures, at −183°, but no quantitative results could be obtained. While each isotherm determined at that temperature was probably as accurate as those obtained at 0°, it was impossible to obtain satisfactory checks. On the other hand, it may be stated qualitatively that the hydrogen adsorptions, in the presence of carbon monoxide at −183°, are decreased by an amount which is approximately equal to the amount of carbon monoxide already present.

Due to the fact that carbon monoxide reacts with nickel, a complete isotherm was never made with that gas at 0°. The amount of carbon monoxide adsorbed at −183° is far in excess of the amount of hydrogen adsorbed at that temperature. Some qualitative experiments indicate that the amount of carbon monoxide adsorbed at 0° is at least equal to, and probably greater than, the amount of hydrogen adsorbed at the same temperature and pressure.

Discussion of Results

It will be noticed at once that the results differ considerably from those obtained with copper by Griffin.[3] On the other hand, at least one point is common to both copper and nickel; namely, a very small amount of carbon monoxide increases the hydrogen adsorption. In the case of copper the increase is noted only at low pressures, for the poisoned isotherm crosses the pure hydrogen isotherm at relatively low pressures; but with nickel the increase can be observed at all pressures up to one atmosphere, when very small amounts of carbon monoxide are employed.

Since it takes only a very small amount of carbon monoxide to cause the increased adsorption, one would hardly expect that such a few molecules could of themselves attract and hold so many more hydrogen molecules. In explaining this increased adsorption, then, it must be assumed that the carbon monoxide changes the surface activity of the adsorbent in some way so as to make more areas available for hydrogen adsorption. There are three ways by which this may be accomplished. Either the carbon monoxide can increase the activity of the already most active areas, or it can stimulate those areas which do not function until higher pressures, or it can create entirely new areas. In view of the fact that only small amounts of carbon monoxide give this effect, the first of the above three ways seems most reasonable to us, because the most active areas have the carbon monoxide adsorbed on them. Therefore, it may be assumed that the increased adsorption is due to an enlargement of active areas, which are produced by having very small amounts of carbon monoxide adsorbed on them.

Griffin explained the decrease of hydrogen adsorption at higher pressures on copper, poisoned with carbon monoxide, by assuming that the carbon monoxide prevented the solution of hydrogen in copper. No decrease in hydrogen adsorption with nickel was observed. However, since the isotherms shown in Fig. 1 draw together at higher pressures, it seems reasonable to assume that at some pressure greater than atmospheric pressure the two isotherms may cross. This drawing together from 1.0 c.c. at 40 mm. pressure to 0.8 c.c. at 700 mm. pressure could be explained by assuming a slight amount, 0.2 c.c., of solubility of hydrogen in nickel. In view of the results of Sieverts[7] this amount does not seem unreasonable.

With the exception of the rate with which equilibrium is reached, it would be difficult to distinguish between the isotherms obtained when larger amounts of carbon monoxide are employed from a pure hydrogen isotherm. Since there seems to be practically no solubility of hydrogen, and in view of the same hydrogen adsorption with or without carbon monoxide present, we must assume that either the carbon monoxide increases the hydrogen adsorbing areas by the amount of carbon monoxide present in each case, or the hydrogen is adsorbed on top of the carbon monoxide as a second layer. In view of the fact that amounts of carbon monoxide in the neighborhood of 0.1 c.c. produce only a very slight increase, if any, in adsorption, we believe that, when larger amounts of carbon monoxide are used, the hydrogen is adsorbed either directly as a second layer, or indirectly through the carbon monoxide as some sort of a surface complex. One might expect this second layer to be taken up slowly, and hence anticipate the much slower, observed adsorption.

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[7] Sieverts: Z. physik. Chem. **60**, 170 (1907).

In conclusion, then, the inhibiting action of carbon monoxide on the hydrogen adsorption of nickel may be pictured in some such manner as this. Extremely small amounts of carbon monoxide produce a slight increase in the hydrogen adsorption; slightly larger amounts, in the neighborhood of 0.04 c.c., produce a maximum increase in the hydrogen adsorption; larger amounts, up to 1.0 c.c, produce decreasingly smaller increases in the adsorption; and still larger amounts of carbon monoxide produce decreases in the hydrogen adsorption. The inhibiting action of carbon monoxide towards the adsorption of hydrogen by nickel might be likened to that group of drugs which have an optimum dose for stimulating body activity, but which produce death in larger amounts. It should be stated, however, that the catalytic activity of a reduced metal does not follow such a course.

It has frequently been pointed out that the relative amounts of gas adsorbed at ordinary pressures by different solids can not be used as a measure of catalytic activity. It has been assumed that only the gas adsorbed at very low pressures is sufficiently activated for catalytic reactions to occur. This hypothesis implies that the more firmly the gas is held, the greater is the degree of activation produced thereby. From the present work and the similar studies of Griffin on copper it might have been expected that carbon monoxide, the presence of which, in very small amount, increases the adsorption of hydrogen at low pressures, would act as a promoter of the activity of the metal, rather than as a poison. Since the reverse is the case, it seems necessary to conclude that the hydrogen, though more strongly adsorbed in the presence of carbon monoxide, is less activated. This must mean that the valence of the hydrogen is largely saturated by the formation of a rather stable surface complex with the carbon monoxide. The poison acts, not by preventing the adsorption of hydrogen on the active areas of the catalyst, but rather by forming a surface compound with those hydrogen molecules which would otherwise have been activated. Depending on the stability of this compound under the given conditions, the action of the poison is more or less pronounced. It should be noted, however, that while the above situation may be fairly general, it can not be universal, since Pease[8] has shown that the adsorption of hydrogen by copper is markedly decreased by poisoning with a small quantity of mercury.

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[8] Pease: J. Am. Chem. Soc., 45, 2296 (1923).

In absence of additional data it would be idle to speculate on the relation between the observations here reported and the peculiarities of copper and nickel as catalysts for the various possible reactions between hydrogen and carbon monoxide.

Summary

A study of the effect of both small and moderately large amounts of carbon monoxide on the hydrogen adsorptions of two samples of reduced nickel has been made at 0° and at −183°.

At 0°, 0.038 c.c. of carbon monoxide increases the hydrogen adsorption at all pressures up to one atmosphere; amounts in the neighborhood of 0.1 c.c. seem to produce only a very slight increase, if any, in the adsorption; and amounts from 0.3 c.c. to 1.6 c.c. have scarcely any effect on the amount of adsorption but decrease the rate of adsorption.

The qualitative result at −183° is that the amount of hydrogen adsorption, at all pressures up to one atmosphere, is decreased by an amount approximately equal to the amount of carbon monoxide employed.

An effort is made to reconcile these results with the known poisoning action of carbon monoxide on the catalytic activity of nickel in hydrogenation reactions.

University, Virginia.

THE APPLICABILITY OF EINSTEIN'S LAW OF PHOTOCHEMICAL EQUIVALENCE

BY B. K. MUKERJI AND N. R. DHAR

We have studied in detail the energetics of fourteen photochemical reactions. From the results now obtained as well as by critically examining the literature on the subject it becomes apparent that Einstein's Law of equivalence fails in the majority of photochemical reactions.

The following fourteen reactions have been investigated with a view to determine the quantum efficiency (number of molecules decomposed per absorbed quantum) in each case at different ranges of the visible and infrared regions of the spectrum and at different temperatures.

(1) Potassium oxalate and iodine; (2) the bleaching of dicyanin; (3) sodium formate and mercuric chloride; (4) quinine sulphate and chromic acid; (5) sodium formate and iodine; (6) potassium permanganate and oxalic acid; (7) ferrous sulphate and iodine; (8) sodium nitrite and iodine; (9) chromic acid and oxalic acid in presence of manganous sulphate and sulphuric acid; (10) sodium potassium tartrate and bromine; (11) mercuric chloride and ammonium oxalate in presence of eosin as sensitiser; (12) the oxidation of iodoform; (13) sodium malate and iodine; (14) sodium citrate and iodine.

The experimental arrangements were the same, as described by Bhattacharya and Dhar.[1]

The following are the experimental results:

(1) *Potassium oxalate and iodine.*

Mean wave length in A°	Quantum efficiencies at		
	20°C	30°C	36°
4725	18.6	40	74.8
5650	3.6	14.9	23.6
7304	3.7	7.5	74

(2) *The bleaching of dicyanin.*

Mean wave-length in A°	Quantum efficiencies at		
	25°	30°	40°
4725	0.258	0.207	0.33
5650	3.36	1.6	2.12
7304	0.29	0.66	0.89

(3) *Sodium formate and mercuric chloride.*

Mean wave-length in A°	Quantum efficiencies at	
	20°	30°
4725	1.2×10^2	6.5×10^2
5650	0.7×10^2	5.6×10^2
7304	0.273×10^2	0.68×10^2

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[1] Z. anorg. allgem. Chem., 169, 381 (1928).

(4) *Quinine sulphate and chromic acid.*

Mean wave-length in A°	Quantum efficiencies at		
	25°	30°	35°
4725	4.3	18.15	3
5650	4	2.66	1.53
7304	2.3	0.45	2.58

(5) *Sodium formate and iodine.*

Mean wave-length in A°	Quantum efficiencies at		
	20°	25°	30°
4725	39	43.8	112
5650	86	14.6	11
7304	54	92	110

(6) *Potassium permanganate and oxalic acid.*

Mean wave-length in A°	Quantum efficiencies at		
	8.5°	14.5°	24.5°
4725	93.8	133	245
5650	38	89	71
7304	39	36	36

(7) *Ferrous sulphate and iodine.*

Mean wave-length in A°	Quantum efficiencies at		
	24.5°	30°	34.5°
4725	18.64	28.4	127.5
5650	16.8	25.7	106
7304	8.34	14.2	52.7

(8) *Sodium nitrite and iodine.*

Mean wave-length in A°	Quantum efficiencies at		
	20°	25°	30°
4725	61.7	190	208
5650	38	81	93
7304	32	68	77

(9) *Chromic acid and oxalic acid.*

Mean wave-length in A°	Quantum efficiencies at	
	21°	31°
4725	53	58.7
7304	3	9.5

(10) *Sodium potassium tartrate and bromine.*

Mean wave-length in A°	Quantum efficiencies at		
	20°	25°	30°
4725	29.4	47	75.3
5650	33.4	36.8	53.3
7304	24.4	26	59

(11) *Ammonium oxalate and mercuric chloride in presence of eosin as sensitiser.*

Mean wave-length in A°	Quantum efficiencies at 26°	36°	46°
4350	35.2	45.4	48
4950	85.1	100.4	154
5400	37.7	42.4	58

(12) *Photo oxidation of iodoform in (a) Amyl alcohol.*

Source of light	Quantum efficiencies at 19°	29°	39°
1000 watt lamp	3.4	3.54	4.05

(*b*) *in benzene medium.*

Source of light	Quantum efficiencies at 24°	34°	44°
1000 watt lamp	450	480	530

(13) *Sodium malate and iodine.*

Mean wave-length in A°	Quantum efficiencies at 30°	40°
4725	27.5	59.7
7304	1.5	5.6

(14) *Sodium citrate and iodine.*

Mean wave-length in A°	Quantum efficiencies at 23°	33°
4725	11.5	14.9
7304	2.6	11.2

Discussion

From the foregoing results, it will be seen that in general, the following two important issues have been dealt with in all these experiments:

(1) The dependence between the photochemical yield and the wave-length of the light employed and (11) the relationship between the quantum efficiency and the temperature of the reacting system.

From the experimental results recorded in this paper it will be seen that the reactions in which Einstein's law of photochemical equivalence is approximately valid are the bleaching of dicyanin and the oxidation of quinine by chromic acid. It seems likely, therefore, that in these two reactions simply the molecules activated by the absorption of energy react and there is no other complicated secondary reaction. We have calculated the heats of reaction of some of these changes from the existing thermochemical data and they are as follows:

(1)	Sodium nitrite and iodine	37661	calories
(2)	Potassium oxalate and iodine	131300	"
(3)	Mercuric chloride and sodium formate	61057	"
(4)	Mercuric chloride and ammonium oxalate	156894	"
(5)	Sodium formate and iodine	55638	"
(6)	Chromic acid and oxalic acid in presence of manganese sulphate and sulphuric acid	294848	"
(7)	Ferrous sulphate and iodine	116151	"

It is clear therefore, that most of these reactions which deviate markedly from Einstein's law are highly exothermal in nature.

Of late years stress has been laid on the importance of the emission of ions and electrons in chemical changes in explaining the mechanism of chemical reactions. From some preliminary experiments we are of the opinion that emission of ions takes place in the oxidation of sodium sulphate by air and experiments are in progress in this laboratory to find out if electronic emissions actually take place in some of the reactions studied in this investigation.

Basing on these observations the following mechanism has been suggested for a bi-molecular reaction.

$X_2 + hv = X_2$ (active .... (I)

X_2 (active) $+ Y_2 = 2XY +$ electron $+$ heat energy ....(II)

Electron $+ X_2 = X_2$ (active) ....(III)

Thus, this view of activation can satisfactorily explain the abnormally large photochemical yield in exothermal reactions.

From our experimental results it will be seen that in most cases the quantum efficiency at different temperatures increases with the frequency of the incident radiation.

It seems probable that this is due to the fact that the total energy of the absorbed quantum goes on increasing with the frequency of the incident radiation and one quantum may activate more than one molecule.

Our results show that in general, the quantum efficiency increases with the increase in the temperature of the reacting substances.

Mukerji, Bhattacharya and Dhar[1] have carried on measurements of the extinction coefficients of some of the reacting mixtures studied in this paper. In every case they found that the absorption of radiation markedly increases with increase in temperature. These results are of importance because they can be utilised in explaining partially the increase of quantum yield with increase in temperature.

Summary

1. The quantum yield of fourteen photochemical reactions have been determined at different temperatures and under radiations of different wavelengths.

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[1] J. Phys. Chem., **32**, 1834 (1928).

2. The Einstein law of photochemical equivalence fails in almost all the cases investigated in this paper.

3. From the experimental results it will be evident that the quantum efficiency gradually increases with the frequency of the incident radiation.

4. The experimental results show that in general, the quantum efficiency increases with increase in the temperature of the reacting substances.

5. It has been proved that those reactions which markedly deviate from the law of photochemical equivalence are highly exothermal in nature.

6. An explanation for the abnormally large photochemical yield has been offered from the point of view of the emission of electrons during chemical changes.

Chemical Laboratories,
University of Allahabad,
Allahabad, November 12, 1930.

THE THERMAL DECOMPOSITION OF CARBON TETRABROMIDE

BY H. AUSTIN TAYLOR

The number of homogeneous gas reactions involving relatively simple inorganic molecules, which up to the present have been shown to occur unimolecularly is extremely small in comparison with the rapidly accumulating number involving complex organic molecules. Two alone in fact are at present known: the decompositions of nitrogen pentoxide[1] and nitryl chloride.[2]

The decomposition of carbon tetrabromide has been shown[3] to occur according to the following equations:

$$2CBr_4 = C_2Br_6 + Br_2$$
$$C_2Br_6 = C_2Br_4 + Br_2$$

with a further possible reaction yielding hexabrom-benzene:

$$3C_2Br_4 = C_6Br_6 + 3Br_2$$

There seems to be some doubt whether the latter possibility does occur; and, if at all, it is certainly to a small extent, the main product being tetrabromethylene. The possibility presented itself that a study of the complete decomposition might yield on analysis a complex rate made up of two consecutive reactions, the first being probably bimolecular and the second, the decomposition of hexabromethane, possibly unimolecular. In view of the work of Stewart and Edlund[4] on the bromination of ethylene, a completely heterogeneous reaction, it was suspected that the decomposition here involved might be in part at least heterogeneous but it was hoped that a measurement of the rate with known surface of contact would allow an estimation to be made of the extent of homogeneity if any were present and permit thereby an analysis of another homogeneous unimolecular reaction. The reaction however was found to be completely heterogeneous and apparently, approximately of first order. The latter is to be expected for a catalysed reaction in which the true order is the second.

The method of following the reaction was essentially a colorimetric one. Measurements were made of the times taken for a known sample of the carbon tetrabromide to yield concentrations of bromine vapor at the temperature of the experiment, sufficient to match certain color standards, the color comparison being made by use of a Lummer-Brodhun photometer head. The color standards were made up from bromine in carbon tetrachloride solution, yielding concentrations in the ratio of 1:2:3 up to six in the six comparative standards used, covering the range of bromine intensity developed by an average amount of carbon tetrabromide. Two sixty-watt lamps were used as sources of illumination, one for the reaction vessel and one for the standards, operated from the same electrical source so that any variation in line voltage would affect each to the same extent.

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[1] Daniels and Johnston: J. Am. Chem. Soc., 43, 53 (1921).

[2] Schumacher and Sprenger: Z. Electrochemie, 35, 653 (1929).

[3] Merz and Weith: Ber., 11, 2235 (1878). See Edgar: Diss. Minnesota (1927).

[4] J. Am. Chem. Soc., 45, 1014 (1923).

The reaction vessel consisted of a pyrex tube of 120 ccs. capacity with flat ends and carrying a small entrance tube at the side through which the solid carbon tetrabromide could be introduced. The reaction vessel was located in the center of a long tubular furnace lying horizontally so that the light passed down the length of the reaction tube to the photometer. Suitable circular diaphragms served to cut out from the light beam entering the photometer, any light passing down the furnace between the sides of the reaction vessel and the sides of the furnace. A glass cell similar to those containing the color standards, but holding carbon tetrachloride alone was used to balance the light intensity passing through the empty reaction tube, the positions of the two light-sources being arranged to this end.

The complete procedure was then to weigh the reaction tube empty, introduce a suitable quantity of carbon tetrabromide,[1] remove the air by evacuation with a hyvac pump for five minutes (longer evacuation was found only to result in removal of the bromide), seal under vacuum at a previously constricted point, and reweigh the tube together with the remainder of the side arm now removed. The difference between the two weights after due allowance is made for the air removed gives the weight of bromide taken. Experience showed that by having the furnace rheostat regulated for the temperature required for the experiment but with the furnace some twenty degrees higher at the moment that the cold reaction vessel was put in place, the furnace was so rapidly cooled and the vessel warmed to the temperature required that little further control was needed to maintain a temperature constant to within ±1.°

The time at which the tube was placed in the furnace was noted as also the succeeding times at which the bromine intensity developed by the reaction balanced each of the six standards. The latter were mounted on a smooth sliding carriage so that each in turn could be moved rapidly into position. By plotting these observed times as ordinates against six equidistant points as abscissae a smooth curve was obtained which cut the time axis at a point close to the origin. The deviation was noted and used as the time required to heat the tube to the temperature in question and vaporize the carbon tetrabromide. This time, in other words, was taken as the starting point of the reaction, the observed time intervals being reduced accordingly. The values quoted are these corrected time intervals.

The results obtained at 300° C. are given in Table I and show the variation of the rate of reaction with amount of the bromide taken.

To determine the approximate order of the reaction the usual test for the time of a certain percentage decomposition may be applied. The times taken for the bromine developed by reaction to reach a certain standard, correspond,

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[1] The author is indebted to Prof. H. G. Lindwall for the sample used, prepared by the bromination of acetone.

TABLE I

Temperature 300°C

Weight of bromide taken	0.3260	0.4488	0.6240	0.9740g.
Standard	Time Intervals in mins.			
1	5.0	4.5	2.0	1.0
2	11.75	9.0	4.0	2.0
3	22.0	16.5	8.5	3.5
4	42.0	29.5	14.0	5.5
5	77.0	45.5	20.5	8.0
6	—	65.0	28.0	10.5

These data are plotted graphically in Fig. 1.

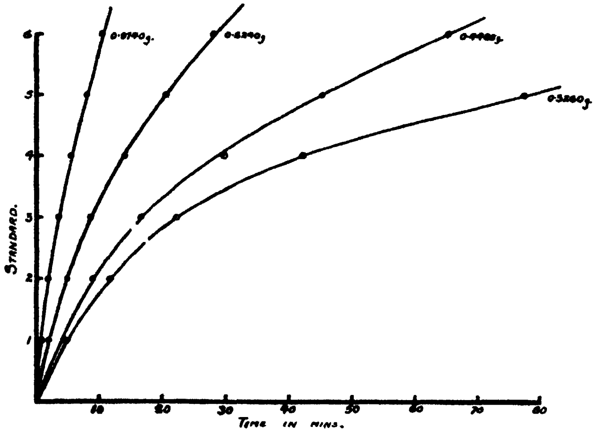

FIG. 1

however, to different total amounts of reaction, when different initial weights of carbon tetrabromide are used. A comparison has therefore to be made between the time taken for one standard to be reached in one case, with the time taken for a different standard in another case depending on the initial amount of reactant used and its rate of reaction. Assuming the reaction to be unimolecular the rate and therefore the concentration of bromide, will be proportional to the initial amount. That is, the amount of decomposition corresponding to the first standard in the first case cited above will be equal to Standard 0.4488/0.3260 = 1.38 in the second case and so on. These times read from the plotted results are in the four cases, 5.0, 6.0, 4.5 and 4.0 minutes respectively, or with standard 2 in the first case and its equivalent in the other cases, 11.75, 13, 12.5 and 11.0 minutes. The order of magnitude of these figures is obviously the same, indicating the correctness of the assumption of first order for the rate. That the agreement is not better is no doubt due to the fact that the reaction is not a simple one and by a disadvantage inherent in the method, the above times correspond to a high percentage total reaction. For measurements to be made early in the course of reaction, extremely dilute standards must be used when the error involved in a photometric balancing becomes largely increased.

The fact that the reaction is not simply that given by the stoichiometric equation soon became obvious after a number of runs had been made in the same tube. The surface of the tube became somewhat blackened with a deposit which was not removed by the ether used to clean out the other products after each reaction. The deposit, probably carbon, negligible in a single reaction, became visible therefore, only after a series of runs had been made in the tube. It was found that after thoroughly cleaning the tube with chromic acid solution, the next reaction tried was several times slower than the ones previously made. It was thought at first that this might be due to some catalytic effect of the carbon deposit. The complete absence of any autocatalytic trend in the rate curves however was significant and the cause was finally shown to be due to reaction between the bromine liberated and the alkali in the glass with the result that the time taken to develop a given visible bromine concentration was increased and the rate apparently reduced. By rinsing the reaction tube, after cleaning with chromic acid and water, with a bromine solution in carbon tetrachloride, reproducible rates could be obtained.

To determine the presence of heterogeneity in the reaction, a thin layer of powdered pyrex was introduced into the reaction tube and after treating with bromine as mentioned above a rate measurement was made. The rate found was so rapid, that it was almost impossible to get a single match with any one of the six standards accurately. The extent of surface was therefore increased less drastically by the introduction of small lengths of glass tubing. The internal surface of the reaction vessel was found to be 190 sq. cms. and an additional surface area of 200 sq. cms. was introduced, the volume being reduced from 120 to 110 ccs. The surface-volume ratio therefore was slightly more than doubled. Table II gives one example of a series of measurements made with this increased surface, the data from Table I using approximately the same initial amount of bromide are included for comparison.

TABLE II

Temperature 300°C.

Weight of bromide taken	0.4325 (increased surface)	0.4488g.
Standard	Time intervals in mins.	
1	2.0	4.5
2	4.0	9.0
3	8.5	16.5
4	14.5	29.5
5	22.5	45.5
6	33.0	65.0

TABLE III

Weight of carbon tetrabromide used = 0.4488g.

Temperature	300	310	320	330
Standard	Time in mins.			
1	4.5	2.0	0.9	0.4
2	9.0	4.0	1.7	0.8
3	16.5	7.0	3.0	1.3
4	29.5	12.4	5.5	2.4
5	45.5	19.0	8.0	3.6
6	65.0	26.3	11.5	5.0

It can readily be seen that the reaction is practically entirely heterogeneous, since a doubling of the surface has doubled the reaction rate.

The effect of temperature on the reaction rate may be seen from the data given in Table III which are the time intervals observed at four different temperatures using approximately the same amount of carbon tetrabromide, corrected proportionately, on the basis of the unimolecular relationship shown above, for the small difference in initial amount taken. The values given therefore are comparable for the mass of bromide stated.

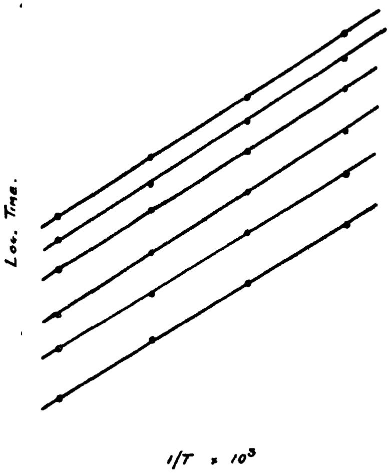

FIG. 2

Fig. 2 shows the linear relation obtained by plotting the logarithms of these times against the reciprocals of the absolute temperatures. The average energy of activation calculated from the above data by means of the Arrhenius equation is 57,200 calories. The value appears to show a slight increase as the reaction proceeds. The average value calculated from the times to the second standard is 55,500 calories whilst that for the sixth standard is 58,300 calories. This would suggest a probably higher activation energy for the secondary reaction than for the primary one, namely for the decomposition of the hexabromethane, which however must also be heterogeneous.

Summary

The thermal decomposition of carbon tetrabromide is shown to be a heterogeneous reaction of apparent first order over the temperature range 300 to 330°C. with an activation energy of 57,200 calories.

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CAESIUM TETRAIODIDE

BY NORMAN RAE

In 1930 a paper was published by Briggs, Greenawald and Leonard[1] on the ternary system caesium iodide, iodine and water at 25°C.

They establish the existence of two polyiodides CsI_4 and CsI_3, and show that the pentaiodide described by Wells and his co-workers[2] does not exist at 25°C.

They call attention to the fact that all other workers in the same field, including the present writer, have followed Wells and assumed that the higher polyiodide is the pentaiodide.

Referring to my paper[3] they say: "Rae studied quantitatively the rate at which iodine is lost by evaporation from the supposed pentaiodide prepared in accordance with the directions of Wells and Wheeler. He gives curves of weight loss against time and shows that the loss virtually ceased, unless the temperature was raised, when the material attained a weight corresponding to the tri-iodide CsI_3. For some unaccountable reason, however, Rae shows no actual experimental data for the first thirty days during which the supposed pentaiodide was losing iodine, nor does he give analyses of the pentaiodide at the beginning of the experiment. Nevertheless, if his weight curve be extrapolated back to zero time, the original composition does come close to CsI_5, but the actual points as given on the curve start out from a stage corresponding almost exactly to a tetraiodide."

The explanation is that the object of the experiment referred to was to show that the break in the volatilisation curve occurs at the point corresponding to the formula CsI_3. Wells and Wheeler give three analyses of their compound in which the percentage of caesium varies from 15.20 to 20.96; from this and the description given, the writer concluded that the supposed pentaiodide was a much more unstable substance than it really turns out to be, and that it would not be possible to prepare the pure dry CsI_5 to give the initial point on the curve. This point was not a necessary one for the object in view and it was a much simpler thing to obtain the composition for the points on the curve from the composition at the end point when only caesium iodide was left.

No attempt was therefore made to analyse the moist product prepared by Wells and Wheeler's method; but, instead, it was placed in the glass weighing bottle in a small desiccator over sulphuric acid to dry for thirty days before transferring to the desiccator containing caustic soda and starting the weighings. The writer was in error in assuming from Wells and Wheeler that the substance was the pentaiodide and that it was more unstable than it really is and, at the time, thought that the pentaiodide had lost iodine over the sulphuric acid at about the same rate as it subsequently did over caustic soda and so the first thirty days were included in the diagram although the curve was not drawn for this period.

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[1] J. Phys. Chem., **34**, 195 (1930).

[2] Am. J. Sci., **44**, 43 (1892).

[3] J. Chem. Soc., **107**, 1286 (1915).

It now appears that the tetraiodide is not a very unstable substance, for the original data are still available and show that after drying for thirty days over sulphuric acid the composition was

	found	calculated for CsI_4
caesium iodide	40·76	40·56
extra iodine	59·24	59·44

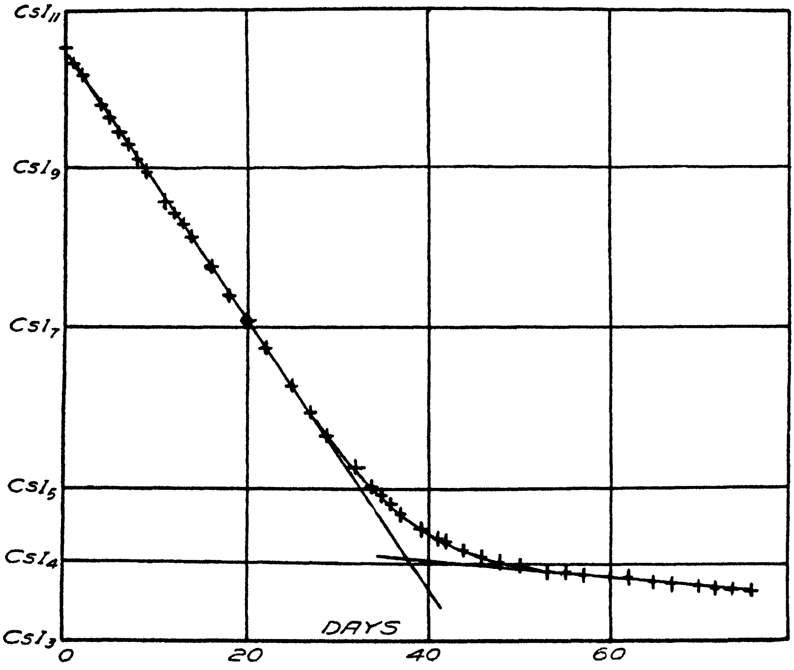

Fig. 1
Caesium Tetraiodide

The authors quoted above also say: "Rae's curves are not very reliable evidence concerning the formulas of the unstable higher polyiodides, since a mixture of iodine and tetraiodide—the supposed pentaiodide—might lose iodine as vapour only very little faster than the tetraiodide alone"; while Wells and Wheeler, in their paper, (loc. cit.) state: "It (CsI_5) loses iodine on exposure about as rapidly as iodine itself volatilises."

To test this statement and also the reliability of the volatilisation method for indicating the existence of a polyhalide, a further experiment has now been made.

Wells and Wheeler found that the higher polyhalide melts at 73°C. and also that artificial mixtures of caesium tri-iodide and iodine, representing compositions varying from CsI_4 to CsI_9, all melt at a uniform temperature of 73°C.

1·7817 grams of caesium iodide were weighed in a flat form weighing bottle, excess of iodine was added, the stopper placed on and the mixture was heated in an electric oven at 80°C. till it had all melted: it was then cooled overnight and weighed to get the weight of iodine added: this was 8.4419 grams. The solid mixture therefore had a composition between CsI_{10} and CsI_{11}. This was placed in a desiccator over caustic soda and was weighed at intervals of two or three days. The caustic soda was renewed three times to ensure that it was not becoming exhausted or coated, thereby affecting the rate of loss. Altogether forty-four weighings were made and these all lie on a very smooth curve which is shown in the diagram. This curve shows a very definite break at the point corresponding to the tetraiodide CsI_4 and also shows that the vapour pressure of the polyiodide is much less than that of free iodine. The average loss per day in the first stage was 0.153 grams and that in the last stage 0.011 grams, that is about fourteen times slower.

Summary

The volatilisation method confirms the correctness of the formula CsI_4 for the higher polyiodide of caesium and shows that its vapour pressure is much less than that of iodine.

University College,
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January 26, 1931.

SOME OBSERVATIONS ON THE COLOUR OF COLLOIDAL SOLUTIONS OF ARSENIC TRISULPHIDE

BY S. S. BHATNAGAR

The paper by Weiser[1] on the subject of the colour of arsenic trisulphide is of considerable interest. It refers in extenso to a paper published by Bhatnagar and Rao.[2] On account of a number of mistakes in translation (as our original paper was written in English) the impression that is left in the mind of the reader is that we consider the red colloidal solution to be definitely As_2S_2. What we actually showed was that the composition of the reddish variety was given approximately by the empirical formula $As_2S_2,x\ H_2S$ and that at one stage of the removal of H_2S, the composition of the precipitate was more nearly As_2S_2 rather than As_2S_3 when the coagulum was obtained out of contact with air. The presence of air as a result of the oxidation of H_2S always increases the percentage of sulphur. The air was avoided in the preparation of our solutions, which does not appear to be the case in the experiments of other authors. Besides the quantities of As_2O_3 originally taken by us for the preparation of colloidal solution are different from those employed by Weiser. That concentrations affect profoundly the physical and chemical character of the coagula is well known (cf. P. P. von Weimarn and others). Moreover this view of ours is in line with the work of Linder and Picton who showed that the results of the analysis of a colloidal solution of arsenious sulphide always gave results for sulphur too low for As_2S_3. Somewhat similar observations were made by Clermont and Frommel.[3] The results of the analysis (mean of several not quite concordant readings) quoted in our paper (loc. cit.) were obtained by Mr. B. L. Rao, M.Sc. and there is no reason to believe that they are wrong in as much as they show a distinctly less amount of sulphur in the composition than would be the case if the precipitate was As_2S_3 entirely.

The senior author of this paper realised long ago that the simplicity of the analytical results obtained by B. L. Rao did not exclude the possibility of their being explained on a formula more complicated than the one proposed in our previous paper. In a thesis (entitled Studies in Magneto-Chemistry submitted by S. L. Bhatia for the D.Sc. degree of the Punjab University, 1928-29) Bhatnager and Bhatia have shown from magnetic data that the formula of the precipitated colloid is more complicated than that originally given by Bhatnagar and Rao.

The author is unable to share the view that the colour of the colloidal solution is due only to variation in the physical character of the precipitated salt. The reasons for this are as follows:—

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[1] J. Phys. Chem., 34, 1021 (1930).

[2] Kolloid-Z., 33, 159 (1923).

[2] Compt. rend., 87, 330 (1879).

1. That even a solution of H_2S in water is not of simple composition, but contains sulphur, pentathionic acid, etc. The presence of these things would certainly add to the complexity of the arsenious sulphide as ordinarily obtained in colloidal form.

2. Winter, Bhatnagar and Rao and Semmler have all noticed evidence for chemical change.

3. The hydrolysis of As_2S_3 or the oxidation of H_2S which result in the ultimate separation of sulphur gives sulphur as well as As_2O_3 a chance to form adsorption complexes which are chemically different from As_2S_3.

4. W. Pauli and A. Semmler[1] regard the colloid as having the constitution $(xAs_2S_3, H_2As_2S_4, HAs_2S_4)H^{\cdot}$.

These views seem to find support from the conductivity and other physical data (W. Pauli: loc. cit). The case is not unique with As_2S_3. Pauli and his co-workers[2] have shown that even colloids like ferric hydroxide have complex chemical composition when their coagula are chemically analysed.

The main thesis of the paper by Bhatnagar and B. L. Rao was to show the complexity of the so-called As_2S_3 solution. While not contesting the experimental work of Weiser, the author ventures to suggest that purely physical aggregates do not explain the complexity or colour changes of those solutions and that the author, as a physical chemist distinctly inclined towards physics, explored the view of Weiser in 1922 without success.

The reason why this work was repeated by Bhatnagar and Bhatia (Thesis, loc. cit.) from the stand-point of other physical properties was that the quantities of the precipitate obtained were so small that more reliance could be put on physical rather than on the purely analytical methods.

The author believes that the aqueous origin of realgar-like material is to be explained along the lines suggested by Bhatnagar and Rao and by Pauli and that chemical complexes are formed and that realgar of aqueous origin is not exactly As_2S_2 but more complex in character, a fact which is borne out by analyses given in books on mineralogy. As_2S_2 formed by igneous methods is sharply to be distinguished from that obtained in the form of aqueous deposits in caves in nature.

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[1] Kolloid-Z., **34**, 145 (1924).
[2] Kolloid-Z., **35**, 131 (1924).

NEW BOOKS

Radiations from Radioactive Substances. *By Ernest Rutherford, James Chadwick and C. D. Ellis. 23 × 16 cm; pp. xi + 588. New York and London: The Macmillan Company; The University Press, 1930. Price: $6.50.* The chapters are entitled: radioactive transformations; the alpha rays; absorption of the alpha rays; some properties of the alpha particle; theories of absorption of alpha rays; secondary effects produced by alpha rays; general properties of the radiations; the scattering of alpha and beta particles; the collisions of alpha particles with light atoms; the artificial disintegration of the light elements; the radioactive nuclei; beta ray and gamma ray spectra; the disintegration electrons; the passage of beta particles through matter; the scattering and absorption of gamma rays; intensity problems connected with the emission of gamma rays; atomic nuclei; miscellaneous.

When discussing radioactive transformation, the authors say, p. 18: "The theory of Cases 2 and 4 has been worked out on the assumption that there is a permanent equilibrium between the successive products of transformation. This is impossible to realise completely in practice, since the amount of every radioactive substance is always decreasing with time. No sensible error, however, is introduced when the *primary* source is transformed so slowly that there is no appreciable change in its amount in an interval of time required for the later products to attain approximate equilibrium with the primary source. This condition is very nearly fulfilled, for example, in the case of radium and its product radon, where the period of the former is 1600 years, and of the latter 3.82 days. The latter approaches its equilibrium value very closely after the radon has been supplied continuously from the radium for an interval of 2 months. During this time, the fraction of the radium transformed is only about 7/100,000, so that for the interval under consideration it may be regarded as a constant source without sensible error. It is convenient to apply the term 'secular' equilibrium to this and similar cases.

"Consider next the important case of radon and its products, radium A, B and C. A stage of equilibrium between radon and its products is reached after the radon has been stored about 5 hours, and the amount of each of the products finally decays exponentially with the period of radon. This is a case of 'transient' equilibrium, for the amounts of the products are changing comparatively rapidly. The amount of radium A, B or C at any subsequent time is always appreciably greater than the amount of secular equilibrium when the supply of radon is kept constant," p. 18.

"The origin of actinium and of its parent protactinium has always been a question of great interest and importance and it is still unsettled. Boltwood early showed that in uranium minerals the quantity of actinium was always proportional to the amount of uranium, indicating that a genetic relation existed between them. On the other hand, the activity of actinium with its whole series of α ray products in a uranium mineral is much less than that shown by a single α ray product of the radium series. The discovery of the new product uranium Y led to the suggestion that it might prove to be the head of the actinium series, for it was present in about the required amount. On this view, the more recently discovered product protactinium is the missing link between uranium Y and actinium. On the other hand, it has also been suggested that actinium has its ultimate origin not in a branch product of the uranium series but in an isotope of uranium existing in small relative amount. It is, however, very difficult to reach a definite decision on these points with the data at present available. Much light may be thrown on this question if it proves possible to purify either actinium or protactinium in sufficient quantity to determine its atomic weight with accuracy. This seems likely to be done for protactinium in the near future, for it exists in uranium minerals in quantity comparable with that of radium and chemical methods of purification have already been devised. When the atomic weight of protactinium is known, the atomic weight of all other members of the actinium series can at once be deduced from a knowledge of the radiations emitted by each product.

"Important new evidence on the problem of the origin of actinium has been recently obtained by Aston (Nature, March 2, 1929, p. 313), by examining with a mass-spectrograph the isotopic constitution of lead obtained from a uranium mineral. A sample of lead, separated by Mr. Piggot of Washington from the radioactive mineral Norwegian bröggerite, was compared with the spectrum of ordinary lead. The mass spectrum of the lead from the mineral showed a strong line 206, a faint line 207, and a still fainter line 208. The line 206 is no doubt due to uranium-lead, but the line 207 cannot be due to the presence of ordinary lead as an impurity or to thorium-lead, for in the mass spectrum of ordinary lead the line 208 is about twice as strong as 207. Aston concludes that the line 207 must be in part due to the end-product of the actinium series, actinium-lead. This, if correct, fixes the atomic weight of all the members of the actinium series. Since six α particles are expelled in the transformation of protactinium into actinium lead, the atomic weight of protactinium should on this view be 231. The atomic weights of the actinium series, given in the table of the radioactive elements, have been calculated on this basis. The evidence indicates that protactinium must arise from an isotope of uranium. The simplest assumption to make is that this isotope, number 92, which will be termed actinium, has a mass 235, and is transformed by the emission of an α particle into a β ray product number 90 which gives rise to protactinium. The β ray product is probably to be identified with uranium Y," p. 32.

"In addition to the groups of α particles which have been assigned to a definite product in the radioactive series, there have been found associated with the complex bodies radium C and thorium C a few particles of abnormally long range. The first observation of these long-range particles was made by Rutherford and Wood in 1916. When absorbing screens sufficient to stop completely the α particles of 8.6 cm. range were placed between a thorium C source and a zinc sulphide screen they still observed a small number of scintillations, which they attributed to an unknown group of long-range α particles. The range of these particles was found to be about 11.3 cm. in air, and their number was about 100 for every 10^6 α particles emitted from the source. They obtained indications that roughly one-third of these particles had a range of about 10 cm., but the evidence was not definite.

"Later Rutherford observed, during the investigations which led to the discovery of the artificial disintegration of nitrogen, that the α particles of radium C were accompanied, in their passage through nitrogen and oxygen, by a small number of particles which had a range in air of about 9 cm. On account of their small number—about 28 in 10^6 of the normal α particles—it has been difficult to fix with certainty the origin and nature of this group of long-range particles. For various reasons Rutherford at first concluded that these particles were not emitted by the source of radium C but arose in the volume of gas exposed to the collisions of the α particles, and suggested that they might prove to be atoms of nitrogen and oxygen set in rapid motion by close collision with an α particle. In later experiments he examined the deflection of these particles in a magnetic field and concluded from his results that the particles probably had a mass of 3 and carried a double positive charge, and that they were indeed isotopes of the ordinary α particles. Subsequently, however, similar measurements of the magnetic deflection of the more numerous long-range particles from thorium C showed that these particles had a mass of 4, that is, were ordinary α particles. This result threw grave doubt on the former conclusions about the nature of the particles from radium C, and further investigation showed that these also were α particles, and, moreover, that most probably they were emitted by the source of radium C and were not produced by collision in the gases traversed by the α particles," p. 87.

"It was observed by Rutherford and subsequent investigators that it was unexpectedly difficult to follow the reduction of velocity below about 0.40 V_0, where V_0 is the maximum velocity of the α particles from radium C, corresponding to a range of α particles of 4 or 5 mm. in air. This difficulty was in part due to the marked heterogeneity of the issuing beam, which caused a broad diffuse band of α particles in a magnetic field, but mainly to the influence of another effect which has only recently been recognised, namely the rapid capture and loss of electrons by low velocity α particles. This effect only manifests itself clearly in a high vacuum, when the issuing beam splits up into three distinct groups of α particles corresponding to neutral, singly charged, and doubly charged particles. With the addition of a small quantity of gas in the path of the rays, these three bands disappear and give place to one main band which is less deflected than the group of doubly charged particles," p. 102.

"We have so far referred to observations on the distribution of He_+ and He_{++} particles after passing through mica and other absorbing screens. An unexpected effect was noted when observations were made with bare sources of platinum wire coated with the active deposit of radium by exposure to radon. Within the limit of experiment, the number of He_+ particles corresponded to an equilibrium distribution. This could not be due to some of the radioactive atoms being driven by recoil into the metal, for a similar effect was observed when a polished metal wire was coated with a surface deposit of radium C by electrolysis. This result is surprising when we consider that on the average the deposit is not one molecule thick and that the mean free path for capture for such velocities corresponds to 3 to 4 mm. of air. It seems probable that the distribution observed is to be ascribed to the radioactive matter itself.

"It is very difficult to believe that these He_+ particles come directly from the nucleus and, even if this be assumed, it is a curious coincidence that the number should be about that required for equilibrium between He_+ and He_{++} in their passage through mica. It was at first thought that a partial equilibrium is set up by the passage of the α particles through the dense distribution of the electrons around the nuclei from which they are expelled. This peculiar effect can, perhaps, be explained by taking into account some recent observations made by Mlle Chamié on the distribution of active matter whether deposited by the action of the emanation or by chemical action. She has obtained definite evidence that the active matter is not uniformly distributed but collects together in granules which may contain as many as a million atoms. Similar results have been obtained by Harrington. Under such conditions, it is easily seen that an approximate equilibrium between singly and doubly charged particles will be set up by the passage of the α particles from the interior of the granules to the surface. The average thickness of these granules is sufficient to lead to an approximate equilibrium between He_+ and He_{++} in the issuing beam of particles," p. 129.

"Taking into account the reduction factor employed in calculating the secondary ionisation, and using the data of Lehmann, it can be estimated that the total ionisations δT per cm. for an α particle of speed corresponding to 1000 electron volts in hydrogen, helium, and air are in thousands of ions 2.9, 2.15, 9.1 respectively, while the observed values are 4.6, 4.6 and 22 respectively. On the average the ionisation calculated in this way is about one-half the observed for all three gases. This indicates that the number of collisions which lead to ionisation are about twice as numerous as those calculated on the Henderson theory, and about 1.5 times the number on the revised theory. A similar result has emerged from a comparison of theory with observation for absorption and straggling of the α rays. The analyses of these different data are thus consistent among themselves and lead to the general conclusion that for the lighter gases the number of effective collisions giving rise to the liberation of δ particles of different speed is about twice as great as that calculated from simple classical considerations, when no account is taken of the orbital velocity of electrons.

"If the classical considerations of the transference of energy between the α particles and electrons are substantially correct for close encounters, the difference must be due to the probability of transfer of considerable quanties of energy in more distant collisions, which on the classical theory gives only a small energy transfer. Such interchanges are possible on the new wave-mechanics and a more complete solution will no doubt ultimately be given along these lines," p. 146.

"The recoil of the atom due to the expulsion of an α particle is clearly observable in a Wilson photograph when the expansion chamber contains a radioactive gas. Photographs of this kind have been obtained by C. T. R. Wilson, Bhose and Ghosh, Kinoshita, Akeuti and Akiyama, and Dee. At ordinary pressure, the recoil track is shown by a knob at the end of the track. As the pressure is reduced, the recoil track becomes longer and often shows evidence of a marked scattering. In some cases, the usual direction of the recoil track does not coincide with the direction of flight of the α particle, but this is no doubt due to a large deflection of the recoil atom by a collision with an atom near its point of origin. The marked ionisation of the recoil atom per unit path is clearly shown by the density of the initial part of its track. Dee has examined the recoil tracks from actinon and actinium A in an electric field in a Wilson expansion chamber and determined the charge and mobility of the recoiling atoms," p. 155.

"When strong sources of radium C, thorium C, or polonium deposited on a small flat plate are viewed in a dark room with a rested eye, the source is seen to be surrounded by a weakly luminous hemispherical zone extending over the range of the *α* particles. This luminosity excited by the *α* rays in gases was first studied by the late Sir William and Lady Huggins, who examined the spectrum of the weak light emitted by radium preparations in air and found it to coincide with the band spectrum of nitrogen. This appears to be due to the *α* ray bombardment of nitrogen occluded in the source. These experiments have been confirmed by a number of observers including Himstedt and Meyer, Walter, Pohl, and Bosch. The spectrum of luminous radium bromide is in part continuous, due to the fluorescence of the crystal. In an atmosphere of helium, a few helium lines were noted but no lines were observed in hydrogen, carbon monoxide and carbon dioxide. The luminosity excited in gases can be best studied by using a source of polonium which emits only *α* rays, and screening the photographic plate from the direct *α* radiation. There seems to be no doubt that the spectrum of the weak luminosity produced by *α* rays is in general similar to that produced by the electron discharge under special conditions in gases at low pressure. Such an effect is to be expected, since the *α* rays cause the same general type of ionisation and molecular dissociation produced in a vacuum tube by cathode rays and positive rays. The luminosity produced by *α* rays, however, under ordinary experimental conditions is exceedingly feeble compared with that produced in a discharge tube. . . .

Plates of mica are rapidly coloured brown or black by *α* rays, the rapidity of coloration depending on the composition of the mica. Geologists long regarded with curiosity small coloured areas in certain kinds of mica, for example, in biotite, cordierite, and muscovite. The sections of these coloured areas are usually circular in shape, and exhibit the property of pleochroism under polarised light, and for this reason were called 'pleochroic haloes.' The centres of these areas usually contain a minute crystal of foreign matter. Joly first pointed out that these haloes were of radioactive origin, and were due to the coloration of the mica by the *α* rays expelled from a nucleus which contains radioactive matter. This subject has been investigated in detail by Joly and his pupils, by Mügge and many others. In homogeneous material, the haloes are spherical with a radioactive inclusion in the centre and often show a well-marked structure consisting of a number of rings. The radii of these rings are closely connected with the ranges in mica of the different groups of *α* rays expelled from the active material. In the complete uranium halo, the outer ring marks the range of the *α* particle from radium C′ (7 cm. in air), and in the thorium halo the range of the *α* particles from thorium C′ (8.6 cm. in air)" p. 179. Poole concludes that the colour changes in mica are due to chemical decomposition of water molecules by the alpha rays and oxidation of the iron in the mica," p. 183.

"We have seen in the foregoing sections that all the elements from boron to potassium can be disintegrated by the bombardment of *α* particles, with the two exceptions of carbon and oxygen. The result of the disintegration is in every case the emission of a hydrogen nucleus or proton. No evidence has been obtained of the ejection of particles of any other type. So far as has been ascertained, only one proton is emitted from the disintegrating nucleus; this appears most clearly from the experiments in the expansion chamber.

"While in some cases, e.g. aluminium, the kinetic energy of the particles after disintegration may be greater than the kinetic energy of the incident *α* particle, in other cases, e.g. nitrogen, it is less. Thus some disintegrations take place with liberation of energy, others with an absorption of kinetic energy. The probability of producing a disintegration with an *α* particle of given energy varies from one element to another. While the information so far obtained on both these points is meagre and indefinite, yet there emerges from the results a distinct difference in behaviour between the elements of odd atomic number and those of even atomic number. In general the protons emitted by the odd-numbered elements are faster and more numerous than those from the even-numbered elements. It will be recalled that the early experiments were successful in showing the disintegration of the odd elements as far as phosphorus, while the disintegration of the even elements was only observed later.

"This difference between elements of odd and even number manifests itself in other ways. Harkins has shown that elements of even number are on the average much more abundant in the earth's crust than those of odd number. Aston has found that odd elements may have at most two isotopes differing in mass by two units, while even elements may have a large number with a considerable range in mass. The conclusion seems to be that the even elements are more firmly built than the odd elements. In the case of the lighter elements the difference between odd and even has been shown by Aston to extend to the masses of the nuclei. Aston's measurements of the masses of the lighter elements are sufficiently accurate to give some indication of the relative stabilities of nuclei. It is generally assumed that the nuclei of all elements are built up from two units, the proton and the electron. The mass of a nucleus is not given by the sum of the masses of the protons and electrons contained in it, as measured in free space, for inside the nucleus the protons and electrons are packed so closely together that their electromagnetic fields interfere and a fraction of their combined mass is destroyed. The mass destroyed appears as a release of energy in the formation of the nucleus, the greater the loss of mass the more firmly are the charged particles bound together and the more stable is the nucleus so formed. The atomic number and the mass number of the element give the numbers of protons and electrons in the nucleus, and an accurate measurement of the mass of the nucleus will give the loss of mass or release of energy in its formation. Aston expressed his measurements of the masses of the elements in terms of the 'packing fraction,' the divergence of the mass of the atom from the whole number rule divided by its mass number. The packing fraction is therefore 'the mean gain or loss of mass per proton when the nuclear packing is changed from that of oxygen to that of the atom in question.' A high packing fraction indicates looseness of packing of the proton and electron, and, therefore, low stability. We are here concerned not so much with the actual value of the packing fraction as in the change of the packing fraction from one element to the next. If we assume that the disintegration of an element consists solely in the ejection of a proton from the nuclear structure, the residual nucleus will be the next lower in the scale. If, as seems very probable from Blackett's experiments, some disintegrations consist in the binding of the α particle and the emission of a proton, the newly formed nucleus will be the next higher in the scale of elements. In either case an element of odd number will change into one of even number. Now Aston's results show that the light elements of odd number have in general a much higher "packing fraction" than those of even number. Thus when an element of odd number changes into one of even number there will be in general a disappearance of mass. This mass may appear as kinetic energy associated with the emitted proton. Thus Aston's measurements afford a general explanation of the high speeds associated with the protons emitted in the disintegration of the odd-numbered elements," p. 304.

"A claim that lead could be transmuted to mercury and thallium in an arc was made by Smits, but after further experiment withdrawn. Reports of transmutations of even more remarkable type were made by Wendt and Irion, who stated that tungsten was decomposed and partly transmuted into helium when, in the form of a fine wire, it was electrically deflagrated; by Riding and Baly, who claimed that helium and neon were formed from nitrogen subjected to cathode ray bombardment; and by Paneth and Peters, who stated that small quantities of helium could be synthesised from hydrogen by dissolving the latter in palladium. The experiments of Wendt and Irion were repeated very carefully by Allison and Harkins, but no evidence of the production of helium was found. The claim of Paneth and Peters was soon withdrawn and the appearance of helium in the experiments received a more prosaic explanation. It was found that a glass surface which has been completely freed from helium by prolonged heating in hydrogen is able to absorb a detectable amount of helium, almost free from neon, from the atmosphere during only a single day's contact with the air; and also that glass (and asbestos) surfaces which do not give off detectable quantities of helium when heated in a vacuum or in oxygen release quantities of the order of 10^{-9} c.c. when heated in hydrogen. In later experiments precautions were taken to exclude the escape of helium absorbed in the glass surfaces, or the diffusion of helium from the air through hot glass, and the possibility was examined of the formation of helium from certain substances under the action of various agents. Under these conditions the results were entirely negative, and no quantity of helium larger than 10^{-10} c.c. was obtained.

"There can be little doubt that the claims which have so far been made of the transmutation of elements by the use of agents other than swift α particles are untrustworthy. In all the cases reported the presence of an element has been mistaken for its creation. On the present views of atomic structure the nucleus of an atom is extremely small and the forces binding together its component parts are of great intensity, corresponding to several million volts. It seems unlikely that the transmutation of elements on a chemical scale, as opposed to the radioactive scale, will be possible until such potentials are also available in the laboratory," p. 316.

"It may be repeated that the collisions to which this result [of ionisation by β particles] refers are those in which the energy loss is of the order of 50 volts. In connection with the straggling of β particles where the important energy transfers are of the order of 1000 volts, it was found that again classical theory predicted a probability of energy transfer about half that found, although in this case the dependence on velocity appeared to be correct. Williams and Terroux have also investigated the probability of energy transfers of amount 5000 to 10,000 volts by observing the frequency of branch tracks. Here also the actual probability of transfer of energy is greater than that calculated on the classical theory and the dependence on velocity is also in disagreement. Since we have seen that to within about 20 per cent. the total loss of energy is given correctly by the classical theory, it is clear that there must be a divergence from theory in the opposite direction for non-ionising collisions. It appears that the energy actually lost in non-ionising collisions is less than one-seventh of that calculated on classical theory," p. 450.

"The study of the penetrating radiation had its origin in the observations of Elster and Geitel and of C. T. R. Wilson that there was always a small amount of residual ionisation in an electroscope. They found that there was a definite transport of charge to the insulated system even after all possible precautions had been taken to reduce electrical leakage over the insulators. The order of magnitude of this residual ionisation corresponded to the production of about twenty pairs of ions per second per cubic centimetre. McLennan and Burton and Rutherford and Cooke found that the ionisation could be considerably reduced by surrounding the electroscope with a thick layer of some material, and they concluded that part of the ionisation must be due to an external penetrating radiation. That the greater part of this effect was due to radioactive material in the ground was shown by McLennan, Wulf, Gockel, Wright and others, who found that the ionisation was reduced when the apparatus was set up over a deep lake. Bergwitz and Gockel attempted to pursue this further by making observations in balloons. If the radiation came entirely from the earth the effect should decrease with height, due both to the increased distance and to the absorption of the air. Hess was the first to obtain definite results by this method, and showed that, while the ionisation decreased slightly up to a distance of 1000 metres, above 2000 metres it began again to increase, and at 5000 metres it was already two or three times the value found at ground-level. This indicated definitely the presence of radiation travelling downwards through the earth's atmosphere, and in view of the possible cosmic origin of the radiation gave a fresh interest and importance to the investigations. These experiments were continued by Kolhörster with improved apparatus and he was able to extend the measurements to a height of 9000 metres. He observed that the absorption coefficient of the radiation increased with altitude up to 7000 metres and then fell sharply. Quite recently he has made other balloon ascents which have confirmed the maximum of the absorption coefficient between 6000 and 7000 metres, but so far no quantitative theoretical explanation has been offered.

"Millikan and Bowen have reported the results obtained from two flights of small pilot balloons carrying recording electroscopes which reached heights of 11.2 and 15.5 kilometres. The average discharge rate above the 5 kilometre level was about three times the rate at the surface. Hess and Kolhörster have pointed out that this rate was less than that to be estimated from their results," p. 485.

"Some remarkable experiments have recently been carried out by Regener in which he was able to detect ionisation at a depth of 231 metres of water below the surface of Lake Constance. He used a steel ionisation vessel of 39 litres capacity filled with carbon dioxide at 30 atmospheres pressure, and the position of the fibre of the electrometer was registered on a photographic plate at hourly intervals. . . . The great extension in our knowledge of the penetrating radiation provided by these experiments will be appreciated from the fact that even the second value at 78.6 metres is beyond the region explored by Millikan and Cameron," p. 488.

"It is extremely unlikely that the very penetrating radiation observed by Regener could be corpuscular in nature, but it is possible that it is true electromagnetic radiation excited in matter by the impact of the high-speed corpuscles which are responsible for the ionisation observed at smaller absorptions. A detailed examination of this view shows that the chief difficulty will be to account satisfactorily for the phenomena in the transition region.

"At present it is not possible to form any definite idea as to the nature of these corpuscles, they might be either electrons or protons. At such high energies as 10^9, volts, electrons and protons have comparable masses and momenta and the chief remaining distinction is the sign of the charge," p. 490.

"The existence of elements representing nearly all nuclear charges between 1 and 92 is a striking and unexpected fact indicating that, whatever the nuclear charge, stable nuclei can be formed between these limits. The remarkable stability of nuclei and particularly even-numbered nuclei is even more emphasized by the existence of a whole series of isotopes over a considerable range of mass. The nucleus appears to survive the introduction of a certain number of additional protons and electrons without any apparent loss of stability. While so far the observed differences of mass between the lightest and heaviest isotope of an element is limited in general to about 10 per cent. or less, it is by no means certain that a more systematic search may or may not reveal the presence of additional isotopes existing in relatively small amount over a still greater range of mass," p. 524.

"The general evidence on nuclei strongly supports the view that the α particle is of primary importance as a unit of the structure of nuclei in general and particularly of the heavier elements. It seems very possible that the greater part of the mass of heavy nuclei is due to α particles which have an independent existence in the nuclear structure," p. 532.

"It has already been mentioned that there are two exceptions to this general conclusion —potassium and rubidium both show a weak β ray activity which is specific to these elements. This fact was discovered by Campbell and Wood in an examination of the activities of the alkali metals. They found that the β ray activity was shown by all potassium salts, whatever their origin, in proportion to their content of potassium. Tests for the presence of an emanation in the substances used gave a negative result, and they concluded that the observed emission of β rays was a property of the potassium atom. The β radiation was more easily absorbed than that from a uranium oxide preparation, giving a value for μ/ρ in tin varying from 27 to 1.1 as against a value of 10 with uranium. Similarly, the β radiation from rubidium was shown to be a property of the rubidium atom. Rubidium gave, weight for weight, about seven times the effect of potassium, but the radiation was much more easily absorbed. Subsequent investigations by Campbell, Henriot, Biltz and Marcus, Hahn and Rothenbach, Hoffman, and others have confirmed the conclusion that the β radiations of these elements are not due to traces of radioactive impurity but to the elements themselves. All attempts to influence the activity of either element by chemical operations, and thus to prove that the activity is due to radioactive impurity, have been unsuccessful. Biltz and Marcus prepared specimens of K_2SO_4 from potassium minerals of different geological ages; the activity of the specimens per atom of potassium was always the same. Hahn and Rothenbach compared the activities of rubidium sulphate of different ages, 21 years old, 11 years, and new. No difference could be found.

"In both cases the radiation is a β radiation; no α rays have been observed. Campbell showed that the rays from potassium were deflected in an electric field in the same direction as the β rays from a layer of uranium oxide. The deflection in a magnetic field was observed by Henriot and Vavon for the rays from potassium, by Bergwitz for the rays from rubidium," p. 541.

Holmes and Lawson "conclude that the half-value period of rubidium is probably about 10^{11} years, and of potassium 1.5×10^{12} years. These estimates were based on the assumption that all the atoms of the element are similar in their radioactive behaviour. On the other hand, it is known that both potassium and rubidium consist of two isotopes of masses 39 and 41, 85 and 87, respectively, and it may be that only one of these isotopes, or possibly a third unknown isotope, is responsible for the β radiation. In the case of potassium, a partial separation of the isotopes was obtained by Hevesy. The heavy fraction was collected and an atomic weight determination by Hönigschmid gave a value 0.005 unit greater than that of ordinary potassium. The activity of this fraction was measured by Biltz and Ziegert and found to be about 4 per cent. greater than that of common potassium. The results are in good agreement with the assumption that the isotope of mass 41 is mainly if not solely responsible for the β radiation of potassium. Since this isotope forms only one-twentieth of the element, it will have, if entirely responsible for the radioactivity, a half-value period of about 7.5×10^{10} years.

"No transformation products either of potassium or of rubidium have so far been detected. Since the emission of a β particle raises the nuclear charge by one unit, potassium should change into calcium and rubidium into strontium. If in potassium only the isotope 41 is radioactive, the product will be a calcium isotope of mass 41; at present only two calcium isotopes are known, of masses 40 and 44. Using the above period for potassium 41, it can be calculated that, since the consolidation of the earth's crust, about 2 per cent. of this isotope will have disintegrated. The maximum amount of calcium 41 which has accumulated in potassium minerals during all geological time will amount therefore to about 0.1 per cent. of their potassium content. Even if a potassium mineral could be found which contained only a trace of calcium, it would be exceedingly difficult to detect the difference in atomic weight between the calcium of the mineral and calcium of other origin. In the case of rubidium, the chemical difficulties in the way of establishing the difference in atomic weight between strontium produced by the decay of rubidium and ordinary strontium would not be so great. On the other hand, there is no real rubidium mineral; this element is widely disseminated over the earth's crust but always in small amounts," p. 543.

Wilder D. Bancroft

The Physical Properties of the Soil. *By Bernard A. Keen. 22 × 14 cm; pp. vii + 380. New York and London: Longmans, Green and Company, 1931. Price: $8.00; 21 shillings.* The chapters are entitled: historical introduction; mechanical analysis; distribution and movement of water in the soil; soil properties at low moisture contents—the field range; soil and clay pastes and their behavior; the properties of soil and clay suspensions; soil constants and equilibrium points; physical properties of soil under field conditions—cultivation and cultivation implements; soil temperature; the soil atmosphere.

"Although numerous histories of agriculture have been written, a wealth of untouched material still remains. In particular, no attempt has hitherto been made to trace the relations between the growth of ideas on the physical properties of soil and the development of cultivation implements. An endeavour to do this is made below, attention being confined primarily to British conditions," p. 1.

"In 1523 Fitzherbert's 'Boke of Husbandry' appeared. The book will always remain famous as the earliest work in the English language dealing expressly with practical agriculture, but it deserves to be also remembered for the acuteness of many of the observations on soil cultivation. Fitzherbert possessed a keenly observant mind, and his facts are given with surprising accuracy, although centuries were to pass before the full explanations could be given," p. 3.

"Although Fitzherbert's main concern was to give detailed technical instructions in adjusting and using the implements for the best advantage, he was, at the same time, forming ideas on the physical properties of soil. He recognized the beneficial effect of frost, and alternations of wet and fine weather on heavy soil laid up in ridges. He was fully aware of the danger of freshly ploughed strong land running down to a hard crust under heavy rain. He stressed the value of keeping a rough, lumpy surface over the winter wheat, for not only did this keep the land warmer, but it prevented weed growth, and in the spring the lumps of soil broke down into finer mould, to the benefit of the corn. The distinction between soil and subsoil was not explicitly mentioned, but he drew attention to certain places in Cornwall and Devon where, if the husbandman ploughed deep, he would 'passe the good grounde and have but lyttel corn,' even though the inevitable mattock was used for breaking down the clods. This type of soil, in Fitzherbert's opinion, was more suitable for grazing than for arable farming," p. 5.

"Further trials showed that draught was very little affected by speed. Pusey was very much interested in this result and discussed its practical application at some length. It explained what had much puzzled him in his tests: the invariably higher draught given on all types of soil by the Scottish plough. This plough had a high reputation, based on the greater area ploughed in a day by the Scottish ploughmen as compared with that done in England. Pusey's tests showed that this merit was not due to the design of the plough, which was inferior to the best English patterns, but to the superior adaptation of the brisk Clydesdale horses used to draw it. Although the plough draught was greater than expected, it did not, of course, increase with speed, and was, in addition, well within the power of the animals, whose greater pace enabled them to plough more in a given time than the English horses," p. 21.

"Since the supreme advantages of steam power were the extra depth of working, and speed of work, was it not right to utilise the second one as well as the first and, by substituting cultivators for ploughs, further increase the effective speed of working by combining into one the two operations of deep ploughing and subsequent cultivation? The query was a legitimate one, especially as the actual operation of cultivation had assumed much more importance with the new husbandry; and besides this, there was some evidence that it might obviate the necessity for drainage operations. The key to the matter lay in the ground itself. In general, deep cultivation would answer so long as the soil was not weedy; in this case the plough was preferable, as it would bury any such growth. In other cases the soil needed the weathering effect of winter on the ploughed furrows to be kept in good tilth," p. 26.

"It was stated in the introduction to this chapter that the promise of an accurate specification of size distribution held out by the elegant experimental methods of Odén and others could not be substantiated, owing to the existence of an inherent source of error in every method so far devised. This error was first clearly brought to light by Coutts and Crowther during the experiments at Rothamsted while the Odén-Keen balance was under construction. They were employing a silt suspension of known concentration, whose particles settled completely in a reasonably short time. Knowing the dimensions of the cylindrical sedimentation vessel, the pan, and its depth below the surface of the liquid, the weight of particles that should have been caught by the pan was easily calculable. In many cases surprising differences were obtained between this weight and that actually measured. Examination by transmitted light of the condition in the neighborhood of the pan disclosed the cause of the error. The particles originally underneath the pan subside, and leave clear liquid behind them, since the pan itself intercepts those particles that would enter the clear liquid. On the other hand, in the annular region surrounding the pan, no such interception occurs. In consequence, there is a constant tendency for the suspension density in this annular region at the level of the pan to be greater than that immediately under the pan. Interchange of suspension between the two regions inevitably occurs, and complicated currents are set up in the fluid which interfere seriously with the free vertical fall of the particles, thus contravening the fundamental assumption on which the whole of the mathematical analysis is based," p. 66.

"The factors causing aggregations of soil particles are the cementation by calcium carbonate, a loose aggregation by organic matter, cohesion between particles, and aggregation analogous to the flocculation of weak suspensions. Preliminary treatment with HCl will remove the first, vigorous mechanical pestling or brushing in water the third, while the fourth is dealt with by adding a deflocculating agent, *e.g.* ammonia, in the International method. The effect of organic matter was studied by Robinson, who suspected that the mechanical analysis of certain Welsh soils by the older British method (p. 46) gave unduly low figures for clay when the field behavior of these soils was considered. He found that a preliminary treatment with hydrogen peroxide decomposed or rendered soluble the non-structural organic matter, thus releasing the fine mineral particles held by it, and the percentage of clay was appreciably increased in the subsequent mechanical analysis. This preliminary treatment is included in the International method," p. 74.

"The Odén-Keen automatic recording balance was developed at Rothamsted to provide a continuous graphical record of the change of weight with time, of a pan suspended in a sedimenting soil suspension. It has been found exceedingly useful for other work—*e.g.* evaporation studies, in which single experiments may extend over a considerable period.

"In the original Odén form, weights were automatically dropped into one pan at the instant that the increasing weight in the other pan caused the balance to tilt. The improvements introduced at Rothamsted consisted in the addition of electromagnetic control for the intervals between successive additions of these weights, and the provision of a device giving graphical record of the changes in current. It was found possible to adapt the well-known Callendar Recorder to serve both these purposes," p. 82.

"The feature of the two preceding sections is the demonstration that water movement and distribution are intimately connected with the geometry of the soil framework. Hence, in order to picture the configuration of the pore space, attention should be devoted primarily to the solid part of the soil, *i.e.* to the soil framework. The irregular shapes and sizes of actual soil particles necessitate recourse to some regular and uniform material for the purposes of theoretical development. We therefore consider the so-called "ideal" soil, consisting of spheres all of the same radius, packed together in a systematic manner," p. 109.

"The salient features of the moisture relations are the quantum-like movements of water associated with the filling and evacuation of cells and the fact that different moisture contents can be associated with a given pressure deficiency, the actual value of the moisture content depending on the manner in which that value is approached. These features and the corresponding pressure deficiencies have been verified experimentally by Haines both for 'ideal' and 'natural' soils in a series of simple and ingenious experiments," p. 121.

"The papers of Tempany and Hardy contain exhaustive accounts, based on measurements of the linear shrinkage of soil blocks from which the volume shrinkage was inferred. Tempany concluded that the space between the mineral particles was wholly occupied by a water-saturated gel-skeleton, whose contraction, when water was lost by evaporation, was manifested by shrinkage of the block. Hardy showed that, apart from the doubtful general nature of this hypothesis, it failed to explain the slight shrinkage of some laterite soils from Barbados. Hardy adopted Wilsdon's view that the colloid material possessed a reticulate or minutely porous structure, and contained water in two phases, one adsorbed in the walls of the gel and the other filling the vesicles of the gel, and concluded that shrinkage was due solely to the loss of vesicular water," p. 137.

"In the field, soils are not normally in the plastic condition described in the preceding section, but have a looser structure. Nevertheless, marked shrinkage effects are shown by heavy clay soils on drying. Deep cracks up to an inch in width at the surface are common even in English clay soils during drought, and much mechanical damage to root systems may result. In clay soils under tropical and sub-tropical conditions larger cracks may develop, several inches in width and several feet in depth. In the older 'basin' system of irrigation in Egypt, the soil, after the winter crop of wheat or berseem, remained from May to August, when the Nile flood waters again became available. The extent of the cracking during the 'sheraqi,' or summer fallow, on a typical square metre of the surface can be seen from Fig. 37. Only the larger cracks are shown; there are numerous smaller ones ramifying in all directions. The work of Mosseri shows that this shrinkage not only improves the tractability of the heavy clay deposits in the Nile valley, but as the soil dries out, the deleterious salts concentrate on the outside of the lumps and are thus washed down by the subsequent irrigation of flood water. Mosseri has stated that this effect has been largely responsible for the past freedom of the Nile valley from alkali troubles," p. 143.

"At the time when the so-called 'adsorption isotherm' was receiving much attention in colloid science, attempts were made to estimate indirectly the amount of colloidal material in soil. Ashley used the adsorption of a dye (malachite green) and Mitscherlich and Floess worked with water vapour. The hypothesis on which these methods were based was soon abandoned, but the methods themselves were revived by American workers in connection with their studies of the 'ultra-clay' extracted from soil suspensions by a high-speed centrifuge. They concluded that the relative absorptions of a dye, ammonia, water vapour, or the heat of wetting, shown by the whole soil and by the colloidal material extracted from it, gave a fair measure of the total colloidal content.

"Joseph has criticised the assumption because these methods often give values for the colloid content exceeding the clay content. This would imply that some of the silt fraction was colloidal, which is unlikely. The explanation suggested is that silt possesses some of the properties (*e.g.* base exchange, heat of wetting) chosen for estimation of the colloidal material, and is thus erroneously included in the latter. Joseph further suggested that the clay content as determined by mechanical analysis should be regarded as the colloidal content also. This view was supported by his observation that with repeated passage of a clay suspension through the supercentrifuge used for collecting colloidal clay, the whole of the clay could be obtained in the colloidal form," p. 170.

"Although the colloidal material is essentially a crystalline bentonite, it is not composed of finely divided unaltered crystals of the original clay mineral, but has suffered change in chemical composition by weathering. Kelley demonstrated this by grinding very finely in a ball-mill actual rock materials, calcium-saturated bentonite, and clay colloids, and determining the exchangeable bases before and after the operation. He found that the other replaceable bases, particularly magnesium, were increased in the case of bentonites and clay colloids, but not in the ground rock material, and concluded that these bases were caught in the meshes of the clay crystals, which were ruptured by grinding, thereby exposing the replaceable loss to base exchange. This difference between the original rock and clays was taken to be a consequence of the weathering processes in soil formation . . . .

"The physical and physico-chemical properties of clay suspensions have been the subject of a great number of experiments in recent years, and a connected account would be a difficult matter even if investigators had come to a general measure of agreement. But the literature abounds in anomalies and contradictions, and there is every sign that this will continue for some time to come. The reason is twofold: the experimental methods of colloid science have, with few exceptions, not yet reached the desired stage of refinement; and, compared with the majority of systems studied in colloid science, the clay particle is exceedingly complex. Apparently unimportant small differences in experimental conditions—often unrecognised, and, more often, not recorded—may profoundly affect the measurements, and, in turn, the conclusions. Perhaps the greatest difficulty, apart from that of preparing clay for experiment in some definite and reproducible state, is that chemical decomposition of the clay complex and base exchange phenomena frequently occur, in addition to the particular effect that the investigator is ostensibly studying. In consequence, phenomena ascribed to the original clay material may really belong to a different complex, and one, moreover, which has probably been changing continuously during the experiment," p. 175.

"The idea that the soil moisture could be regarded as distributed in a thin continuous film over and around the soil particles was generally held at the end of the last century; in 1897 Briggs gave it a definite physical form, and treated the films from the standpoint of the surface tension over their curved surfaces, using the ideal soil as his model. The films were convex outwards over the surfaces of the particles, and concave outwards at the points of contact of the particles. Moisture gradients produced by evaporation or percolation were thus analogous to changes in film curvature, or, what amounted to the same thing, changes in the thickness of the films. Movement of soil moisture from regions of high to low water content, and its equilibrium distribution under any given conditions, could therefore be treated as a matter of the resultant force of surface tension over surfaces of varying curvatures, and of gravity. The treatment, in fact, was closely modelled on the classical work of Reinold and Rücker on soap bubbles, which is familiar to all physicists.

"Owing to the omission of one step in his chain of reasoning—apparently minor but, in reality, vital—Briggs missed the really important consequence of his hypothesis, and thirty years were to elapse before Haines gave the correct version (Chapter III, Section C). As developed by Haines, the geometry of the ideal soil was used to define the characteristics of the pore space, and this, in turn, served to specify the configuration of the water films. Briggs omitted the intermediate step, and referred the water film directly to the soil particles," p. 203.

"Alway and Shull made further criticisms with special reference to the wilting-coefficient. The former showed that if the atmospheric conditions were modified, plants would not wilt until the soil moisture was reduced nearly to the hydroscopic coefficient. Shull's work showed that the plant wilted although the amount of soil moisture and the osmotic pressure gradient from soil to root were in its favour; the explanation of the wilting was that evaporation continued from the leaves largely independent of conditions in the soil. The work of these two investigators demonstrated that the wilting-coefficient depended on the physiological behavior of the plant and the atmospheric conditions, as well as on the soil-water relationships," p. 208.

"In preparing soil for shrinkage determinations, the mass is kneaded with successive additions of water until it shows signs of becoming sticky or fluid. The point at which the mass is just not sticky or adhesive to the fingers is well defined and can be determined accurately after a little practice. It can be regarded as the moisture content at which the attractive power of the soil for water is just satisfied, and is now generally referred to as the 'sticky-point.' The determination was advocated by Hardy, who considered that it measured the maximum imbibitional capacity of the soil colloidal material for water," p. 220.

"There are good reasons for the inclusions of the sticky-point in any scheme of 'single value' measurements for soils. It is a measurement with definite physical significance, and is highly correlated with the ignition loss—in itself a desirable measurement—and it provides a measure of the water held by colloidal material and the interstitial water, the latter having a reasonably constant value for a very wide range of soils," p. 226.

"Meanwhile there arises the fundamental question as to the origin or cause of the variations in soil resistance. What has led to the apparently fortuitous and erratic variations shown in the typical isodyne maps of Figs 57, 60-62? The key is to be found in the observation that they remain constant from season to season. They are almost certainly the resultant of the age-long soil-forming processes. For example, drainage would not proceed uniformly over a field. Small differences in the degree of packing of the particles, minute differences in contour of the surface, would have a cumulative effect on the physico-chemical composition, which would be demonstrated by differences in properties of the kind discussed above. The whole gamut of geological, climatic, and vegetative factors are concerned, and to these must be added the progressive changes brought about by man in his agricultural operations. With the exception of the latter factor, therefore, the isodynes may be ranked with the observations made on soil profiles in the modern system of soil classification," p. 256.

"By destroying weeds cultivation obviously conserves soil moisture. There is also a widespread belief among practical men that the creation of a loose, dry mulch on the soil surface by frequent cultivation prevents loss of water from the underlying moist soil. The effect is ascribed partly to the poor heat conductivity of the dry layer keeping the underlying moist soil at a lower temperature and thus reducing its rate of evaporation, but mainly to the interruption of capillary rise of moisture which, but for the loose dry layer, w[illegible]d reach the surface and evaporate continuously. There is also a third effect, which is [illegible] much mentioned in the literature but is of importance on moist, medium, and heavy so[illegible] in humid climates. This is the tendency to form a surface cap or crust in a dry spell following heavy rain. It is most noticeable in the spring, and the delicate roots of young plants are often injured when the soil contracts into a crust. Cultivation breaks and loosens the surface layers before they have dried out and thus prevents crust formation," p. 271.

"Veihmeyer's extensive results in large tanks and field plots under a wide range of conditions also showed that no appreciable conservation of moisture was secured by mulching. Rotmistroff reached the same conclusion from his studies at Odessa. On the other hand, King, Hilgard and Loughridge, Cameron and others concluded that upward capillary movement of water to the surface was responsible for considerable losses that could only be prevented by maintaining a dry soil or other mulch at the surface.

"The divergence of opinion can be largely but not wholly resolved. Upward capillary movement of water is now known to be effective over short distances only (p. 93). Hence the conception of a mulch as breaking the capillary channels and thus preventing water from actually reaching the soil surface is invalid, unless a permanent or temporary water table exists within some 6 ft. from the surface. Examination of the experimental conditions used by the above workers shows that in nearly all cases where no benefit resulted from mulching, no water table existed near the surface; conversely, mulching did conserve moisture if such water table existed," p. 273.

"Russell and Appleyard showed that after the soil air was evacuated it was possible to remove a further quantity of gas, consisting largely of CO_2 with some nitrogen. They suggested that this dissolved atmosphere came from the colloidal material in the soil. Winogradsky has shown by a direct microbiological technique that both aerobic and anaerobic conditions exist in soil that is in good physical condition and well aerated. This observation is quite consistent with our picture of the structure of a soil in good tilth, and a rough general idea of the conditions can be attempted.

"The soil particles are aggregated into compound particles or sponge-like crumbs, lying loosely together. The pore spaces between these aggregates are of the same order of dimensions as the compound particles themselves, and this would allow free movement of air and of water. Within the compound particle, however, the dimensions of the pore spaces are in all probability much smaller, as many of the individual particles forming the crumb are very minute. The exterior surface of the compound particle may be regarded as perforated with very small holes communicating with the interior. Owing to the capillary phenomena these minute pores would always tend to be closed with water, and this effect would be aided by such portions of the colloidal material that swell in water. Many of the compound particles therefore could, for a time, develop anaerobic conditions in the interior, although surrounded by fully aerobic conditions," p. 353.

Wilder D. Bancroft

The Development of Physiological Chemistry in the United States. *By Russell H. Chittenden. 23 × 16 cm; pp. 427. New York: Chemical Catalog Company, 1930. Price: $6.00* In the preface, p. 7, the author says: "In the following pages the attempt has been made to show by explicit statements of actual experimental accomplishments, at different times and in different places, by many workers and groups of workers, something of the progress which has been made in this country during the past half century in the field of physiological chemistry. . . Critical analysis of the accomplishments recorded here has not been attempted; care has been taken to avoid playing the part of a critic of either work or workers."

Some of the sub-heads are: standing of physiological chemistry and physiology in this country in 1870-1880; establishment of the first laboratory of physiological chemistry in the United States; early lines of experimental work; study of proteins; establishment of a department of physiological chemistry at Columbia University; studies at the University

Pennsylvania; chemistry of the brain; chemical study of the tubercle bacillus; specialization in physiological chemistry; physiological chemistry at Yale; vitamines; internal secretions.

The studies of Atwater and Benedict with the "respiration-calorimeter confirmed many of the findings of European physiologists and at the same time gave added data of physiological value for the solving of problems in nutrition. Thus they showed that the heat produced by a man in a given period of time is the same in quantity as that which can be derived from the energy liberated in the oxidation of food materials during the same period; that the energy which a man expends at hard work, is the exact equivalent of the energy liberated by the body metabolism. Their results confirmed the views held by physiologists generally that the energy of muscular work comes mainly not from the oxidation of protein matter, but from the oxidation of carbohydrates and fats, thus affording added proof of the incorrectness of the old theory that protein was the sole source of the energy of muscle work. Especially noteworthy is the fact that these investigations demonstrated for the first time on *man* the application of the principle of the conservation of energy to the human organism," p. 58.

"In contrast to the 14-18 grams of total urinary nitrogen, which must be looked on as normal if the Voit and Atwater dietary standards are followed, Folin pointed to his analyses of normal urines which showed a daily total nitrogen varying from 4.2 to 8.0 grams from a man, perfectly normal, who had for years subsisted on a low nitrogen diet, and 3.8 to 6.5 grams, 3.6 to 6.7 grams and 2.8 to 5.3 grams of urinary nitrogen per day in three other individuals fed on a starch and cream diet. The important matter, however, connected with these figures was the peculiar distribution of the urinary nitrogen. Thus, on a protein-rich diet Folin found 86-89 per cent of the nitrogen was in the form of urea, while on the protein-poor diet the urea-nitrogen had dropped to as low as 62 per cent of the total.

"Again, it was observed that where the protein metabolism was reduced toward the minimum, creatinine-nitrogen was markedly increased, in one case even to 11 per cent of the total nitrogen. These and other facts led Folin to the conclusion as a principle in the chemistry of metabolism, that *the distribution of the nitrogen in urine among urea, and the other nitrogenous constituents depends on the absolute amount of total nitrogen present.* Folin deemed the part played by creatinine as a factor in the relative distribution of the urinary nitrogen the most interesting feature of these investigations and he was led to adopt as "another fixed principle in the chemistry of metabolism" the fact that the *absolute quantity of creatinine eliminated in the urine on a meat-free diet is a constant quantity different for different individuals, but wholly independent of quantitative changes in the total amount of nitrogen eliminated,*" p. 80.

"Intermediate products between proteins and acid-albumin, however, may be produced by the action of acids. Thus, Osborne found that if crystallized edestin was dissolved in the least possible quantity of hydrochloric acid and then precipitated by addition of a small amount of sodium chloride, the precipitate could not be wholly dissolved in a strong solution of the salt. In other words, a portion of the original edestin had been converted into an insoluble form which could not be made soluble again in a neutral salt solution. Further, as it was not soluble in dilute solutions of potassium hydroxide it could not be acid-albumin. Since practically all seed proteins behave in this manner, Osborne has suggested for such insoluble products the general term 'proteans."

"Especially interesting was the observation made by Osborne that the acidity of edestan chloride was three times that of edestin chloride; i.e., that the basic property of this altered product was much greater than that of the protein from which it was formed. Toward alkalies the vegetable proteins are more resistant. Thus, Chittenden and Osborne (1891) found that zein, even when exposed to the action of a two per cent solution of potassium hydroxide at 40°C., for twenty-four hours, did not lose its original solubility in alcohol, although it is possible an 'alkali albumin' soluble in alcohol may have been formed," p. 102.

"Again, it is to be remembered that with the exception of man and the anthropoid ape, uric acid is not the main end-product of purine metabolism in the mammalia, the urine containing an oxidation product of uric acid, *viz.*, allantoin. When allantoin is abundant, uric acid is correspondingly diminished. Further, in those animals which excrete relatively large amounts of allantoin certain of the tissues have the power *in vitro* of converting uric acid into allantoin. As a result of these conditions, the oridinary breed of dog, for example, oxidizes the larger portion of the uric acid formed in the metabolic processes, also destroying the greater portion of any uric acid given subcutaneously," p. 138.

"Especially noteworthy were Stanley R. Benedict's results obtained in an investigation of the metabolism of Dalmatian coach dogs, 1916-1917. This breed of dogs proved to have a very peculiar purine metabolism, in that, as Benedict found, they excrete relatively large amounts of uric acid even on a purine-free diet. Thus, with one dog of this breed, weighing about ten kilograms on a diet containing only 2.03 grams of nitrogen there was an excretion of 0.154 gram of uric acid nitrogen and 0.073 gram of allantoin nitrogen, with a total nitrogen output of 5.4 grams. Further Benedict found that the excretion of uric acid showed no gain when the nitrogenous food was increased fourfold, although the output of allantoin increased as the nitrogen intake was augmented," p. 139.

"In searching for a chemical explanation of antiketogenesis, Shaffer made the suggestive discovery that while hydrogen peroxide oxidizes aceto-acetic acid slowly in an alkaline solution, the addition of glucose to the mixture causes the aceto-acetic acid to disappear rapidly, the rate of disappearance increasing with increase in the amounts of glucose and alkali. In strongly alkaline solution at 38° C. with an excess of glucose and hydrogen peroxide the oxidation is complete in a few hours. Glucose was thus shown to possess in alkaline solution *in vitro* a ketolytic action in hastening the oxidation of aceto-acetic acid, which, as Shaffer stated, 'appeared to be analogous to its antiketogenic action in the body.' Glycerol and fructose were also found to be ketolytic, while lactic acid had no such power," p. 188.

"Bloor's investigations of the distribution of lipoids in the blood in various diseases have given interesting results, but only a brief reference can be made here. In acute experimental anemia in rabbits, it was found that of the phosphoric acid compounds of the blood, the lipoid phosphorus was most noticeably affected by the lipemia which resulted. Values as high as five times the normal were observed in the plasma, and twice or over the normal value in the corpuscles. It was also noted that when the lipoid phosphorus was at these levels in either plasma or cospuscles, there was an accompanying increase in inorganic phosphate, which would seemingly imply some relationship between inorganic phosphorus and the lipoid phosphorus," p. 204.

"Apparently all soluble salts of manganese increase liver autolysis, due, as Bradley believed, to an alteration of the normally resistant fraction of the liver proteins, by which they become digestible by the protease. He found that further foreign proteins, such as casein and peptone, as well as the coagulated liver proteins, are digested by the autolytic enzymes of the liver, but this was not true of the crystallized vegetable protein edestin, unless manganous chloride was present. Ovalbumin, on the other hand, could not be digested by the liver except in the presence of hydrochloric acid," p. 208.

"That the reaction, both sensitization and intoxication, must be due to the protein molecule seems perfectly certain, since it is quite inconceivable that any admixture having sufficient potency could be present in the injected protein, where such small amounts are employed, as to produce the effect noted. Again, the experiment with egg albumin affords a good illustration of the well-known fact that both sensitization and intoxication may result from the action of one and the same protein molecule. In such case the question arises as to whether the whole protein molecule is active in accomplishing both sensitization and intoxication, or whether one part of the molecule is responsible for the sensitization while another part causes the intoxication.

"Many attempts to answer this and similar questions have been made without any convincing result. If, as has been claimed by several workers in this field, the intoxication that follows the second injection of protein into animals that have been sensitized by a previous injection is due to a cleavage of the protein molecule with liberation of toxic groups, it is conceivable that the intoxicating effect may be the result of some action on the part of the aromatic radicals of the protein molecule. The work of Wells has brought to light many interesting facts bearing on this question, some quite new, some simply confirmatory of the work of others.

"Thus gelatin, the poorest of all proteins in aromatic radicals, was found to be lacking in the ability to participate in the anaphylaxis reaction, either with itself or with other proteins; animals sensitized to egg whites did not show any symptoms when injected with a solution of gelatin and conversely did not sensitize to egg white. Again, gliadin with its low content of tyrosine and phenylalanine was found to be weak in either intoxicating or sensitizing properties, presumably the former. Pure zein, on the other hand, was actively and specifically toxic to guinea pigs sensitized with zein, although this protein is lacking in both tryptophane and lysine. Plainly, the aromatic radical tryptophane does not take any part in the intoxication produced by proteins, or at least is not an essential factor.

"However important the individual amino-acids may be in contributing to the anaphylactic properties of proteins, it is evident that it is the protein molecule as a whole that is antigenic; when the protein molecule is broken down, the fragments are without antigenic action. Thus, as Wells has found, even such large molecules as the proteoses, peptones, and polypeptides are without the power to either sensitize or intoxicate guinea pigs whether used in conjunction with themselves or with undigested egg white. Likewise, the crystallizable amino-acids were similarly inactive. In other words, as soon as proteins are altered or decomposed to any extent beyond the coagulable form their anaphylactic properties disappear," p. 236.

"Among the proteins of vegetable origin, the so-called proteoses obtained by Osborne from different seeds and grains were found by Wells and Osborne to be distinguishable by their biological reactions as well as by their chemical behavior. They possessed strong anaphylactogenic properties, causing very severe anaphylactic intoxication when injected into sensitized guinea pigs, even in doses of 0.001-0.0005 gram, such doses proving fatal with some of them. Further, their activity was not destroyed by heating at 100° C. for one-half hour. These so-called proteoses are clearly chemically and biologically distinct from the other vegetable proteins so thoroughly studied by Osborne, the anaphylactic intoxication they produce greatly exceeding that induced by the reserve proteins of seeds in general. As stated in an earlier chapter these so-called vegetable proteoses must be quite different from the proteoses formed in pepsin and trypsin proteolysis, since the latter are not possessed of any anaphylactogenic properties whatever.

"The work of Wells and Osborne with isolated pure proteins has strengthened belief in the view 'that the antigenic capacity of a protein depends on the entire large colloidal molecular structure, while its specificity seems to reside in certain of the radicals of the molecule.' The older belief that the immunological specificity manifested by individual proteins must be due to differences, too slight to be detected by any known method, either chemical or physical, has given way to the conviction that 'immunological differences between proteins are usually, and as far as now known always, associated with and presumably dependent upon chemical differences which can be detected by chemical or physical methods.' To this view the work of Osborne and Wells has contributed much, but while admitting that the specificity of the anaphylaxis reaction is connected with the chemical structure of the protein molecule, there remains the question what groups or radicals are concerned in these extremely delicate immunological reactions, where traces of protein almost unbelieveably small are able to produce such startling physiological results," p. 239.

"In the latter study [by Mann, Wilhelmj and Bollman] it was found that when glycocoll and alanine were introduced intravenously into normal dogs, a definite specific dynamic action was produced with the usual change in the excretion of nitrogen through the urine, such as ordinarily follows the injection of amino-acids; but when the liver was removed, glycocoll and alanine failed to produce this effect.

"In their study of glycogen, it was observed that in dehepatized dogs the glycogen of the muscles decreased proportionally to the decrease of blood sugar; that when glycogen was introduced intravenously it was converted into glucose and utilized by the hypoglycemic animal. 'The symptoms which appear with a definite hypoglycemic level (0.035 to 0.025 per cent) bear no relation to the absolute amount of glycogen in the muscles and appear while there is still sufficient glucogen to bring the blood sugar to normal if it were released.' In other words, the glycogen of the muscles cannot be drawn upon rapidly to sustain the normal level of sugar in the blood. Hence, it follows that the liver must be the main source of glucose in the blood and that the muscles of the body are of very little, if any, help in the maintenance of the normal content of blood sugar," p. 285.

"The evolution of physiological chemistry, as in the development of most branches of science, has naturally been attended by more or less specialization, resulting in a tendency towards limitation of one person's activities to some particular branch or section of the science. In the earlier years a worker might range from one field to another with reasonable success; he might indeed become proficient in the entire domain of physiological chemistry. Today, however, all this has changed with the rapid development of the past thirty years, and the individual worker must of necessity limit his activities to some special field in which he may hope eventually to become especially proficient and perhaps a recognized authority," p. 287. "Truly hyperspecialization in many directions is a necessary concomitant of progress today in physiological chemistry," p. 289. The reviewer wonders whether this is necessarily true.

"Though the student and practitioner of medicine today must of necessity be fairly well trained in chemistry, indeed must depend upon chemistry for much knowledge of which he stands in need, yet no one in this generation would think, of advocating the establishment of chairs of chemistry in a medical school. Such a procedure would truly be archaic. Wherein is physiological chemistry in any different position? It is true that physiological chemistry, or biochemistry if that term is preferred, is giving first aid in the solving of many problems of great physiological and pathological importance, but so too are chemistry and physics. It may be said that many problems of a chemical nature present themselves which only the well-trained medical man can appreciate the bearings of, but if such problems are to be solved accurately the one undertaking the investigation must be equally well trained in chemistry, otherwise failure is bound to result. It is certainly as practical for the well-trained physiological chemist to cope with such problems, through study of the special medical aspects of the case, as for the medical man to acquire the necessary knowledge of and experience in the use of the chemical procedures called for," p. 323.

Wilder D. Bancroft

Infra-Red Analysis of Molecular Structure. *By F. I. G. Rawlins and A. M. Taylor. 22 × 14 cm; pp. xv + 176. Cambridge and New York: The University Press; The Macmillan Company, 1929. Price: $3.50.* In the preface the authors say: "It is noticeable that no book in English exists which deals with the application of infra-red spectroscopy to the analysis of molecular structure. This fact made itself evident to us a few years ago at the outset of work in this region of the spectrum, and it is for this reason that we offer our book —with all its failings—to others who may undertake investigations upon molecular physics, and who approach the subject from the point of view either of the mathematician or of the physical chemist.

"The theme is that of the interchange of energy between matter—gaseous, liquid and solid—and infra-red radiation. With the properties of such an energy flux we are but little concerned, and this serves to explain the omission of much that is interesting in the verification of different radiation formulae, and in the ramifications of pyrometry. Actual laboratory procedure for the circumscribed purpose in view claims a chapter to itself, whilst a selection of the most important mathematical conceptions—again strictly limited to the immediate aim—forms an appendix," p. v.

"Since the infra-red radiation consists of electromagnetic oscillations of a frequency which is slow compared with the normal rate of motion of electrons in atomic orbits, emission and absorption will only occur for charged masses moving at speeds which are some hundred times slower than electron velocities. These masses consist in general of charged ions. Thus the utility of the infra-red radiation lies in the fact that it gives a method by which the presence of rotating or vibrating doublets can be detected," p. x.

"In an important paper Czerny, using a modification of Rubens' original method, was able for the first time to observe the pure rotation spectrum of a diatomic molecule (HCl).

He used a diffraction grating and found no less than seven bands between 42μ and 100μ, which show almost constant differences of wave-number," p. 12.

"Schaefer and Philipps have investigated carbon dioxide gas within the range of frequencies accessible with prisms of quartz, fluorite, and rock salt. Bands of high intensity are found at 2.72μ, 4.25μ, 14.87μ, and it is probable that these are due to fundamental modes of vibration. Now a triangular form, if isosceles, has three characteristic oscillations, and hence the supposition is that CO_2 is a very thin isosceles triangle. . . . Eucken brings forward, from chemical and thermodynamical quarters, evidence which suggests that Schaefer and Philipps' results are compatible with a linear form," p. 22.

"The three gases NH_3, PH_3, AsH_3 have formed the subject of an extensive research by Robertson, Fox and Hiscocks. Their results for NH_3 agree in the main with those of Schierkolk, though the detail was carried to a greater degree of refinement. If the view propounded by Hund be accepted, that NH_3 is a tetrahedral molecule with N at the summit, it is impossible to bring the observed bands into line with his scheme of fundamentals and overtones. That the three gases possess very similar structures is shown by the remarkably constant ratios which persist between the positions of corresponding bands (see page 26)," p. 25.

Allibone has done some work "on the so-called 'many-lines' spectrum of hydrogen. It will be remembered that this peculiar spectrum is really the band spectrum of the hydrogen molecule. The reason for its unusual characteristics is that the moment of inertia is so small as to mask the ordinary appearance," p. 37.

"In explosions of coal gas and air, as much as 25% of the energy of the flame and explosion is liberated in the form of infra-red radiation, the partition of which among the scale of wave-lengths is a function of temperature. Absorption of infra-red radiation in front of the flame is not a dominant factor. In a mixture of hydrogen and oxygen, for example, emission (flame) bands are found to which no absorption bands are known to correspond. It may however be otherwise in some cases. When CO and O_2 are exploded, some 30-50% of the total radiation from the explosion lies in the 4.4-4.5μ band. Now Coblentz found that a thickness of 5.7 cm. of CO at atmospheric pressure absorbs about 40% of incident radiation for this band, from which it may be inferred that some pre-heating is present in advance of the CO flame. This might be considered as almost auto-catalytic in effect. David has produced evidence of pre-activation by infra-red radiation from a study of CO-air and CH_4-air reactions. According to his researches, the speeds of explosion are accelerated if immediately before explosion the gaseous mixtures are insolated by infra-red radiation corresponding to the absorption band of the gas. This acceleration takes place towards the end of the explosion, when a compressional wave has set in advance of the flame. A 'duration of life' of several seconds is suggested for molecules of CO and CH_4 under these conditions, which is in agreement with the energy distribution in flame and explosion spectra.

"A number of recent observations by Garner, Johnson and Saunders upon catalytic effects in CO and O_2 explosions (moist and dry) and infra-red emission spectra may be mentioned. Water and other positive catalysts greatly reduce the emission at 4.4μ and 2μ to 8μ; whilst up to the present no contrary effect of increase of infra-red emission has been observed. The authors however remark that the possibility must not be overlooked that catalysis in the flame and explosion is always of this type," p. 38.

"There is a great prevalence of absorption bands of liquids in the visible spectrum, a number of which are probably connected in some way with those of the infra-red. It is hardly likely tha Haber's rule will apply, since this really amounts to the assumption of simple harmonic motion. Victor Henri expresses the opinion that the infra-red and ultraviolet frequencies of a liquid are connected by integral relationships, and that this simple character is maintained when a number of bands are present in either region. This amounts in effect to a general acceptance of Haber's square-root rule, or some similar formula," p. 46.

"Collins, using two spectrometers to obtain high dispersion, has worked between 0° and 95°C. in order to find out the nature of the shift with temperature. He establishes a displacement towards shorter wave-length with increasing temperature, and a marked increase of the intensity of absorption for the bands at 0.77μ, 0.98μ, 1.21μ. This latter effect is described as due to the presence of varying amounts of the polymers $(H_2O)_2$ and $(H_2O)_3$ at different temperatures.

"In a recent contribution Tammann reports the outcome of some extensive researches on the 'water' band at 4.7μ. He finds that this band is very strong in ice, lacking in water-vapour, present but weak in water and much reduced in a concentrated solution of NH_4Cl. The cause is ascribed to changing quantities of the species $(H_2O)n$, as in Collins' examination," p. 48.

"A common microscope cover-slip of thickness 0.09 mm. showed absorptions at 5.5μ and 6.52μ which correspond fairly closely with well-known bands of SiO_2. A specimen of glass only 0.001 mm. in thickness showed a transparency of 90% up to 8μ. This affords an interesting comparison with the behaviour of glass of 'ordinary' thickness, i.e. that of electric lamp bulbs, which is usually opaque to infra-red radiations well on the shorter wave-length side of 3μ. With the very thin piece, Coblentz examined the reflection spectrum, and found a number of considerable maxima near 9μ. When the composition of the melt was altered the intensity varied a good deal, but little effect was recorded upon the positions of the bands. This appears to be in general agreement with what is found for ordinary liquid solutions, in which concentration seems to have little influence on band displacement," p. 59.

"What exactly the relation of the water groups to the radicle groups may be is an interesting though obscure question, but Schaefer has pointed out that this water of crystallization possesses a kind of mimicry, in the sense that it becomes uni-axial in uni-axial crystals, and bi-axial in bi-axial ones: in other words it appears to assume the optical character of its surroundings. A detail which has not up to the present been settled is the relationship of the intensity of these water bands to the number of molecules of water of crystallization present. An interesting case for research would be that of copper sulphate, which at different temperatures holds different numbers of molecules of water of crystallization," p. 62.

"Lindeman has suggested a means by which the frequency may be determined at the temperature of melting. If the atoms in a space lattice are vibrating, then the amplitude can never exceed the lattice spacing, and the attainment of this limiting condition is then characteristic of the melting temperature," p. 82.

"It may be as well to notice here the bearing of the ionic or non-ionic nature of the groups upon the type of infra-red spectra obtained. In the case of polar salts where the units are unquestionably ionic, such as NaCl, KBr, etc., the forces are so related to the masses that the vibration is a slow one lying far out in the infra-red spectrum. In the case of groups like CO_3, NO_3, SO_4, etc., where the charges borne by the central atom can be quite large, the infra-red spectrum always shows the presence of comparatively rapid vibrations, usually corresponding to wave-lengths from 6μ to 15μ or 20μ. This undoubtedly indicates that even though the central atom may exert very great polarizing power upon the external atoms of the group, thereby largely modifying the forces of cohesion and consequently the periods of characteristic vibration, yet the atoms are fully ionized and act upon one another with the ordinary coulomb forces, which are sufficiently strong to account for the rapidity of the fundamental or characteristic oscillation.

"Thus the type of infra-red spectrum may be made a valuable criterion of the nature of the forces within the complex radicles, and consequently of the state of ionization of the component parts. Such an argument may even be extended to a non-metallic compound such as silicon carbide, where intense reflection bands are found in the short infra-red region, which may thus be taken as indicative of the ionic nature of the units Si and C, one having a negative charge the other a positive charge, in spite of the family resemblance between the two atoms. In the following paragraph evidence is mentioned for supposing a similar behaviour even among the atoms of the element sulphur," p. 104.

"Within the last few years it has become increasingly clear that Newtonian mechanics, even assisted when necessary with relativistic refinements, are incapable of describing the states of molecular and atomic systems. In other words, the quantum theory needed a new mechanics suitable for systems of the order of magnitude met with in modern physical research.

"The first attempt in this direction was due to Heisenberg, and resulted (the mathematical machinery being in part due to Born and Jordan) in the matrix mechanics. The basic idea was that only directly observable quantities such as intensity and frequency should find place in a rational theoretical physics, and thus the possibility of knowing the history of an electron in a stationary state (i.e. where it does not radiate) was frankly abandoned," p. 147.

"Thus, in the same way that it becomes unjustifiable to apply the methods of geometrical optics when obstacles and apertures become comparable in their dimensions with the wave-length, Schrödinger considers the breakdown of particle mechanics for distances of the order of molecular or atomic dimensions. This view ascribes the failure of the cruder treatment in both cases to the fact that both light and matter originate in wave motions (compare equation $g = v$ above)," p. 149.

Wilder D. Bancroft

The Colloid Chemistry of Rubber. *By Paul Stamberger. 25 × 16 cm; ii + 80. London: Oxford University Press, 1929. Price: $2.00.* This book contains the subject-matter of the Gow Lectures given at University College in November 1928. The subjects of the five lectures were: colloid chemistry and colloids; the colloidal properties of rubber—rubber latex and its industrial applications; lyophile colloids (gels)—crude rubber and its solvation; compounding—compounding ingredients—rubber substitutes—synthesis of rubber; vulcanization—devulcanization—recent views on the structure of rubber.

This is a disappointing book because the author does not say anything definite. On p. 18 we read that "in the natural latex we find that the particles vary in size, mostly from 0.1 to 2 μ." There is nothing to show that this is not a haphazard variation, that it depends on the species, and that the latex with the small particles cannot be precipitated readily by centrifuging.

In one paragraph on p. 24 the author has the latex coagulating at pH 4.8 and in the next paragraph at pH 6.6. There is a good deal of question nowadays whether the rubber in the latex is liquid or not. On p. 36 the author says: "In the case of swelling the solvation action of the solvent on the jelly is not sufficiently strong to disintegrate the whole solid, and it combines with it at first, by penetrating between the particles of the solid, separating them from each other to a certain extent and thus increasing the volume.

"In this manner the jelly imbibes solvents. The nature of forces between jelly and liquid has not yet been fully investigated. Katz suggests that in both cases the same forces are present, and does not see much difference between the swelling of a jelly and the solution of a crystal. Other workers, such as Zsigmondy and Kruyt, put forward the hypothesis of adsorption. With the experimental data available at present it is hardly possible to decide which of the theories is correct. It is not impossible that in some cases both phenomena occur, in others one of them only," p. 36.

On p. 40 the author cites von Schröder's experiments with gelatine to show that a gelatine jelly swollen to its maximum, when taken from the liquid and placed in a closed space containing the saturated vapor of the solvent, loses a part of its liquid. He is distinctly supercilious about the apparently contradicting observations by Wolff and Buchner. On p. 44 the author assumes that a solution of killed rubber is a true solution.

"With regard to the colloidal properties of vulcanized rubber, the first question is whether the vulcanized rubber is a two-phase system or not. The possibility of the existence of such a sulphur-rubber dispersion or a rubber-compound rubber dispersion has been mentioned. The vulcanization has been followed under the microscope by E. A. Hauser and Hünemörder; but it is not possible to draw any definite conclusions from this investigation," p. 66.

"The author thinks that the existence of long-chain molecules is the main factor responsible for the behaviour of rubber, which behaviour may be due to a particular aggregation of them. Since crude rubber is in a metastable condition, the circumstances under which it exists will govern the details of its behaviour," p. 76.

The book cannot be recommended. *Wilder D. Bancroft*

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